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COOKIES & CO_2 & CORDUROY

were the ingredients of this unlikely mystery. Stains on the pastel shades started it. The finisher blamed the dyer, the dyer blamed the bleacher, the bleacher said oil on the knives did it, and the boss weaver put the finger on the chemist. He couldn't find a patsy—until he found that the spotted goods had all gone through the number three treadle-brush. When the machine checked out clean, he set one of his men to play Pinkerton on the operator.

That's when the real story came out: the oldtimer on the brush didn't have a tooth in his head—but he loved cookies with his lunch. Being without dentures, he had to take a swig of "tonic" to soften every mouthful. Unfortunately, the soda pop was sometimes warm and the CO_2 pressure was just too much for him—so the pinwale going through the machine at noon got a spray of cookies-in-coke. (The problem was solved once for all by the personnel man and a local dentist.)

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MAY 1961
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TEXTILE RESEARCH JOURNAL

Experiments on Wool from Copper-Deficient Sheep

Part III: The Action of Trypsin on Oxidized Wool

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Abstract

The action of trypsin on oxidized normal and copper-deficient wool has been examined by (i) N-terminal-residue estimations and (ii) paper electrophoresis and chromatography on the tryptic digests. Trypsin readily solubilizes oxidized wool but does not digest it completely, probably because of its high cysteic-acid concentration. Little difference was found between normal and copper-deficient wool, although the latter gave a smaller amount of a certain group of acidic peptides. Preliminary tests on the chromatography of the tryptic digests using ion-exchange resins are reported.

Introduction

The large physical abnormalities of wool from sheep fed a diet that is deficient in copper may, it has been proposed [4, 5], be associated with a decrease in the proportion of a certain sulfur-rich protein fraction in the fiber. As already mentioned in Part I [5], the experiments which led to this proposition were suggested by investigations on the action of enzymes on the two sorts of wool. Some of these investigations are described here. The differences between normal and copper-deficient wool revealed in this way are very small, but the experiments on the action of trypsin are described in detail because some of them may be of importance for further investigations on the structure of wool proteins.

Pure trypsin does not attack wool or hair unless disulfide groups have been removed or the structure disrupted in other ways [8]. Oxidized wool fibers, for example, are completely dissolved, except for about 3%, by a 0.003% trypsin solution at pH 8 in about 15 min. at 30° C., although enzyme action continues for much longer. Since merino wool contains about 800 μmoles/g. of arginine plus lysine residues, i.e., about a tenth of the total number of residues, a tryptic digest should contain, if the enzyme exerts its usual specificity [2, 10, 17], a mixture of peptides with an average of 10 residues each and arginine or lysine at the C-terminus.

Tryptic digests of oxidized wool were investigated in two ways: first, the N-terminal residues liberated by the action of the enzyme were identified and their concentrations estimated by Sanger's method [21]. It was found that the enzyme did not act quite as expected. Even after allowing for losses during estimation, the total number of N-terminal residues was less than 800 μmoles/g., so the peptides were longer than expected. The reason for

this is not certain, although the high concentration of cysteic acid residues may have hindered digestion [1]. Normal and copper-deficient wool appeared to be digested to the same extent and no significant difference could be found in their N-terminal residue concentrations.

The second method of investigating the tryptic digests consisted in attempting to separate the peptide mixture by a combination of paper electrophoresis and chromatography—the "finger print" method of Ingram [11]. The digests were found to be very complex mixtures but they appeared to be simpler than would perhaps be expected from the known and suspected heterogeneity of wool. The patterns for normal and copper-deficient wool were very similar although the latter had a lower proportion of a certain group of negative peptides.

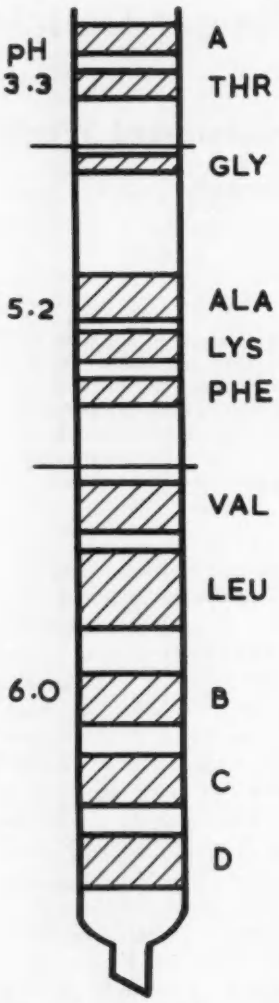

Fig. 1. The separation of DNP-amino acids on a Celite column. Band A contains DNP-aspartic acid, DNP-glutamic acid, and DNP-serine. Bands B, C, and D are artifacts. D is probably dinitroaniline and C dinitrophenol.

Methods

Oxidation and Tryptic Digestion of Wool Samples

The normal and copper-deficient wool samples were some of those the growth and properties of which have been described previously [3, 5]. Merino D5 was a non-copper-deficient wool of medium fineness. The Lincoln wool used was of unknown origin.

The wool samples (0.200 g. of known moisture content) were oxidized as already described [5], i.e., with 5 ml. of a performic acid mixture at 4°C. The acid was removed by allowing the sample to stand *in vacuo* over sodium hydroxide for 6 days or longer. Oxidation for 15 min. was possible for N-terminal-residue tests, but in view of measurements on the oxidation of the cystine residue [5] 4.5-hr. oxidation was used for the subsequent separation of peptides.

After oxidation, the wool samples were shaken at 30° with 10.0 ml. of a 1% sodium bicarbonate solution for about an hour to wet them thoroughly. Then 10.0 ml. of a fresh trypsin solution in 1% sodium bicarbonate was added. This contained either 0.006% of salt-free trypsin or 0.012% of $MgSO_4$-trypsin; in either case the reaction mixture was approximately 0.003% with respect to trypsin. The mixture was then shaken gently at 30° for 6 hr. or longer depending on the tests to be undertaken. Digestion for 6 hr. was used for N-terminal-residue studies and for 24 hr. or longer for the separation of peptides. The undigested residue, which contained impurities not removed during washing as well as fragments of the cuticle, was centrifuged off and weighed. It was usually 3% or less of the original wool. The tryptic digests were usually stored at $-10°$ if necessary.

Twice-crystallized trypsin from Worthington Biochemical Corp., Freehold, N. J., was used. Lot 641 was used for most tests, although lot 571, which contained about 50% of magnesium sulfate, gave similar results.

The volatile solvents used were of a technical grade and were distilled before use.

The Estimation of N-terminal Residues in Tryptic Digests

A portion of the digest (usually 2.0 ml. containing about 20 mg. of the original keratin in 1% sodium bicarbonate solution) was dinitrophenylated by shaking at 30° for 8 hr. with 2 ml. of ethanol and 0.15 ml. of fluorodinitrobenzene in a 40 ml. glass test tube [21]. After reaction, the mixture was extracted by decantation with ether until no more yellow material was removed. The aqueous layer was then acidified with dilute hydrochloric acid and again extracted with several changes of ether. The residual ether was boiled off, and 2 ml. of water and 5 ml. of pure 10 *N* hydrochloric acid added making the solution approximately 6 *N*. The tube was then sealed up and the mixture hydrolyzed by heating in an oven at 103° for 11 hr., unless otherwise stated. Tests showed that neither the presence of sodium chloride in the acid solution nor varying the hydrochloric acid concentration from 5 *N* to 8 *N* affected the results.

After the acid hydrolysate had been diluted with an equal volume of water, extracted 3 times with ether, and the ether allowed to evaporate, the ether-soluble dinitrophenyl (DNP)-amino acids were separated by partition chromatography on buffered "Celite" columns [15]. A more elaborate system was necessary than that used previously for DNP-wool [3] because the hydrolysates contained almost all possible DNP-amino acids in widely different amounts.

The ether-soluble DNP-mixture was separated on a composite column of Celite, 15 cm. long and 1.4 cm. in diameter, eluting with water-saturated chloroform. The top 3 cm. of this column was buffered at pH 3.3; the next 5 cm. at pH 5.2, and the bottom 7 cm. at pH 6.0. The separation illustrated in Figure 1 was usually achieved. It was necessary to scrape out the upper bands when they were sufficiently resolved before separating DNP-valine and DNP-leucine. This system shows temperature variations and it works best at about 22–26°.

All work on DNP-derivatives was done in artificial light since it was found that even in acid solution all the DNP-amino acids are unstable in strong daylight. The DNP-amino acids were extracted from the Celite bands and made up to standard volume as before [3]. Concentrations were measured at 360 mμ, and the derivatives were identified by paper chromatography.

If the separation of DNP-alanine, di-DNP-lysine, and DNP-phenylalanine was not satisfactory, they were combined and, after measurement, extracted into ether for separation on a 10-cm. pH 8 column eluting with a water-saturated mixture of chloroform and *n*-butanol (75:25). On this column the bands ran in the order: di-DNP-lysine, DNP-phenylalanine, DNP-valine, and, at the top, DNP-alanine. According to paper chromatography, the di-DNP-lysine contained a small amount of di-DNP-tyrosine. DNP-leucine probably contained DNP-*iso*leucine.

The acid-soluble DNP-amino acids were separated by paper electrophoresis. After the ether had been evaporated off, the acid solution was made up to standard volume and a suitable portion (5 to 10 ml.) evaporated to dryness before being applied in water as a 7-cm. line across the center of a strip of Whatman 3MM paper. Electrophoresis was carried out for 3 hr. at 15 V/cm., in the conventional horizontal apparatus described in the next section. The electrolyte consisted initially of a 1% sodium bicarbonate solution of total volume about 550 ml., although it became more alkaline as electrophoresis proceeded. Separation was improved by filling the apparatus with paraffin (see next section). The separation is shown in Figure 2, in which band X contained acid-resistant DNP-peptides. The bands were cut out of the dry paper and the DNP-derivatives eluted with 0.1 *N* hydrochloric acid and measured at 360 mμ as usual.

DNP-proline was sought in the ether extract from a DNP-tryptic digest after hydrolysis for 8 hr. in 12 *N* hydrochloric acid, but was not detected. This was expected because apparently trypsin does not attack the sequences lys. pro or arg. pro [9, 10].

No corrections were applied to the results apart

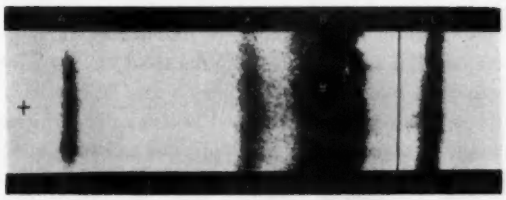

Fig. 2. The separation by paper electrophoresis of the acid-soluble DNP-derivatives from a DNP-tryptic digest of merino wool (E12). The bands are, from positive to negative: DNP-cysteic acid (A), acid-resistant DNP-peptides (X), εN-DNP-lysine (B), and DNP-arginine (C). This photograph was taken by transmitted light so that the bands show the fibrous structure of the paper.

from that for the moisture content of the original wool; although if it was necessary to pass the DNP-derivatives through more than one column the total amount was measured before the second separation and this was divided amongst the constituents by proportion.

Because of its instability, DNP-glycine was estimated separately after 3-hr. hydrolysis.

In order to determine whether any ether-soluble peptides or amino acids were liberated by the enzyme, the ether extracts of the DNP-digest before hydrolysis were examined by the chromatographic procedure used for the ether-soluble DNP-derivatives isolated after hydrolysis. Small quantities of ether-soluble DNP-amino acids and peptides, about 10% of the total after hydrolysis, were found, but the mixture was very complex and was not investigated in detail. No di-DNP-lysine was found.

Tests on pure trypsin solutions of the concentration used for digesting wool showed that autodigestion of the enzyme produced a negligible amount of N-terminal residues.

Electrophoretic and Chromatographic Separation of Peptides

The procedure used was based on that of Ingram [11, 12] who successfully separated a mixture of peptides from hemoglobin on thick paper by electrophoresis in one direction and chromatography in the other.

Whole sheets of Whatman 3MM paper (46 × 57 cm.) were used for two-dimensional separations. The wool sample, after oxidation for 4.5 hr., was digested with trypsin for from 24 to 30 hr. at 30° C. A small portion of the digest, containing the equivalent of 4 or 5 mg. of the original wool, was applied as a spot in one corner of the paper, usually 7 cm. from adjacent edges, by successive 100-microl. applications from a micropipette (100 microl. of digest contained about 1 mg. of original wool). The paper was then folded at right angles 4 cm. from each of the opposite edges and placed horizontally on a rectangular glass frame (59 × 37 cm.) across which a nylon thread was strung for additional support. The folded ends of the paper were dipped into polythene troughs (59 cm. long, 9 cm. wide, and 4.5 cm. high) which were divided to give, as usual, an electrode compartment and a compartment for the paper; electrical contact being made by agar-KCl bridges. Carbon electrodes with platinum contacts were used. The troughs, with frame and paper, fitted inside a large polythene or perspex tank (67 cm. long, 50 cm. wide, and 11 cm. high) which was closed by a glass plate. Horizontal glass cooling coils rested on ledges 4.5 cm. from the top of the tank and were thus suspended a few centimeters above the paper. After the troughs had been filled with the appropriate buffer solution and the paper had been wetted, by capillarity sometimes assisted by spraying with a pipette, the troughs were levelled and the tank filled with paraffin (b.p. 170°) to above the level of the cooling coils in order to prevent evaporation from the paper. For most two-dimensional separations about 10 volts per cm. of paper was used. Improved separation was obtained by using 35 volts/cm. but unfortunately a high-voltage rectifier was not always available. Electrophoresis could be done in the long direction of the paper, if necessary, by using another glass frame and a second pair of troughs.

The buffer solutions used for electrophoresis were those of Michl [14] and Sanger and coworkers [20]. The pH 3.5 buffer consisted of water : pyridine : acetic acid in the proportions 178 : 2 : 20 by volume; and that of pH 6.4 consisted of the same solvents in the proportions 178 : 20 : 2.

After electrophoresis, the paraffin was drained off the tank and the paper dried in an oven. For two-dimensional separations, the paper was then run by descending paper chromatography using one of the systems: (A) *n*-butanol : acetic acid : water (2 : 1 : 1 by volume) and (B) *n*-butanol : acetic acid : water : pyridine (3 : 1 : 4 : 4 by volume). These were adapted from the systems of Ingram [11] and Waley [23].

The most consistently successful method of detecting the peptides after separation and drying consisted in dipping the paper in a 0.3% solution of ninhydrin in acetone containing 1% of water and 0.1% of collidine, and then heating it at 80° for about 10 min. Some peptides were not detected until a few days after this treatment. Another disadvantage was that the intensity of the spots was inversely related to the size of the peptides. Methods in which the paper had to be sprayed with aqueous solutions were difficult to apply because some of the peptides were very soluble and were apt to diffuse rapidly. The Rydon and Smith method [19] was sometimes used to be certain that the spots revealed by ninhydrin corresponded to peptides and not

to amino acids, although there was usually little doubt about this. The method of Reindel and Hoppe was useful for neutral and basic peptides but less successful for acidic peptides [18].

The Elution of Peptides from Paper and the Measurement of Peptide Concentration

The relative amounts of peptides in the groups of bands obtained by the electrophoretic separation of wool digests on paper could be measured approximately as follows: duplicate separations were done on a single strip of paper and after one half had been cut off and treated to reveal the positions of the bands, the corresponding places were cut out of the other and the peptides eluted with 0.5% sodium bicarbonate solution by the usual capillary method [6]. The peptide solutions were then made up to standard volume and the concentrations estimated on 1.0-ml. portions by the Folin-biuret method as described previously [5, 13]. A Beer's law curve, which was non-linear, was constructed by measurements on solutions that had been diluted from the tryptic digest of a known weight of oxidized wool.

Paper that had been washed chromatographically with 0.1 *N* hydrochloric acid and then with water was preferred for experiments on the elution of peptides. Tests showed that relatively large amounts of peptides (500 microg.) could be eluted from the paper almost quantitatively, but that there were large losses in attempts at eluting small amounts.

Experiments and Results

The N-terminal Residues in Tryptic Digests of Oxidized Wool

The effect of duration of oxidation on the N-terminal residues liberated by trypsin was first examined. Table I gives the results of duplicate estimations of the amounts of N-terminal residues liberated by 6-hr. tryptic digestion of merino wool (D5) after oxidation for periods of 15 min. and 17 hr. Each column refers to a separate wool sample. It is clear that 17-hr. oxidation caused no large addition to the N-terminal residues liberated by trypsin so that peptide hydrolysis, if it occurred during oxidation, did not affect the results. On the other hand, some of the N-terminal residues show a *decrease* in concentration; particularly that of serine. The serine residue is known to react in formic acid by taking part in N,O-acyl shift [7], or, more probably, ester formation [22], which could account for these results if a susceptible ser.–arg. or ser.–lys. bond became resistant to trypsin after esterification. It is therefore apparent that prolonged oxidation is undesirable for N-terminal-residue measurements, even if all the disulfide groups have not been removed; oxidation for 15 min. was normally used.

The effect of the duration of acid hydrolysis on the estimation of DNP-amino acids in DNP-tryptic

TABLE I. N-Terminal Residues Liberated by Trypsin from Merino Wool after Oxidation for Different Lengths of Time

Amino acid	N-terminal-residue concentration, μmoles/g. Merino wool (DS) oxidized for: 15 minutes (i)	15 minutes (ii)	17 hours (i)	17 hours (ii)
Asp	17.3	17.3	20.0	16.3
Glu	40.2	40.2	31.6	35.0
Ser	31.8	31.0	17.4	17.4
Thr	30.3	32.5	27.1	26.3
Gly*	27.4	27.4	20.4	
Ala	30.8	31.5	28.6	26.9
Val	17.3	21.9	21.1	21.6
Leu	48.6	41.7	60.1	52.7
Lys	6.4	5.9	5.5	2.5
Phe	3.3	4.8	3.0	3.7
Arg	23.1	22.5	23.9	21.1
$CySO_3$	13.3	12.6	14.4	13.6
εN-Lys	197	165	193	171

* Acid hydrolysis for 3 hr.; the others were for 11 hr.

TABLE II. The Effect of Duration of Acid Hydrolysis on the Estimation of N-Terminal Residues in Tryptic Digests of Oxidized Wool. Lincoln Wool; 15 Minute Oxidation; 6 Hour Digestion

Amino acid	DNP-derivatives, μmoles/g., after acid hydrolysis for: 3 hours	11 hours i	11 hours ii	19 hours i	19 hours ii
Asp	17.5	14.0	14.5	12.2	12.8
Glu	34.7	38.8	33.4	30.7	32.0
Ser	27.0	21.2	20.5	14.8	19.3
Thr	25.0	27.2	27.4	25.4	24.6
Gly	21.8	11.9	10.3	4.2	4.2
Ala	31.1	29.3	25.0	23.2	21.0
Val	12.0	22.2	18.1	19.6	18.0
Leu	44.3	51.0	41.6	40.4	34.1
Lys	4.0	5.1	5.0	4.4	4.6
Phe	3.1	2.5	7.3	3.3	3.5
Arg	18.8	18.0	20.4	20.4	20.1
$CySO_3$	18.5	13.7	12.6	13.5	12.1
Pep*	56.6	50.0	39.6	30.6	34.4
εN-Lys	106	121	128	129	122

* Acid-resistant DNP-peptides.

digests is shown in Table II for samples of Lincoln wool. Other fibers behaved similarly. These figures have been included because they illustrate an unusual feature, namely, the presence of a large amount of "acid-resistant" DNP-peptides. In calculating the concentrations of these, it was assumed that the molar extinction coefficients at 360 mμ were the same as those of the DNP-amino acids. They were present in similar amounts in all the samples studied after hydrolysis for the same length of time and appeared to have similar properties. A much longer period of hydrolysis, about 48 hr., was necessary to hydrolyze them completely, and serine then appeared to be the predominant N-terminal residue. The presence of these acid-resistant DNP-peptides makes it difficult to assess the total recovery of εN-DNP-lysine and the total concentration of N-terminal residues. This should not, however, affect the comparison of results for different sorts of fiber because they were always hydrolyzed under the same conditions.

Difficulty was experienced in deciding the most suitable length of time for tryptic digestion. This is important because of the danger of resynthesis or unspecific hydrolysis if digestion is continued for too long. Application of the ninhydrin method of Hirs, Moore, and Stein [10] suggested that liberation of amino groups from oxidized wool by trypsin was complete in 6 hr. Measurements on the rate of liberation of N-terminal residues showed that, although reaction was almost complete in about 6 hr., further digestion caused a slight increase in the amounts of most of the N-terminal residues. It is difficult to decide if this increase represents unspecific hydrolysis or hydrolysis of very stable bonds adjacent to arginine or lysine residues. The presence of such bonds would be expected from the high concentration of cysteic acid in oxidized wool. Nevertheless, for the comparison of N-terminal residues in similar wool samples, it was thought safest to use a 6-hr. digestion. A longer period of digestion was, however, used for experiments on the separation of peptides, as discussed later.

Table III gives the N-terminal-residue concentrations, after tryptic digestion, of samples of oxidized normal and copper-deficient merino wool from one sheep (E12). Enough results were available for a statistical comparison, so coefficients of variation and standard errors are included. It is clear that any differences in the N-terminal-residue concentrations of these samples are within the experimental limits. Similar, though less complete, results have been obtained for wool from two other sheep (E4 and E9). The results for N-terminal glycine in Table III are of interest because of the indication from earlier work that copper-deficient wool contains much more of this amino acid than normal wool, the difference being about 3 μmoles/g. [3]. No significant difference in N-terminal-glycine concen-

TABLE III. N-Terminal Residues in "Normal" and "Copper-deficient" Wool from Sheep (E12), after Oxidation for 15 Minutes and Tryptic Digestion for 6 Hours

	N-terminal residues, μmoles/g.							
	Merino (E12) normal				Merino (E12) Cu-deficient			
Amino acid	Mean	No. of estimations	Coeff. of variation	Standard error	Mean	No. of estimations	Coeff. of variation	Standard error
Asp	18.7	5	6.9	0.7	18.2	4	12.6	1.3
Glu	36.1	5	8.9	1.6	35.7	4	1.3	0.3
Ser	31.6	5	7.4	1.2	30.0	4	18.8	3.3
Thr	33.8	5	12.7	2.2	31.9	4	6.8	1.2
Gly	30.4	4	4.2	0.7	31.5	5	5.8	1.1
Ala	31.4	5	4.3	0.7	33.5	4	2.7	0.5
Val	18.8	5	8.4	0.8	17.4	4	9.4	0.9
Leu	68.1	5	9.7	3.3	68.7	4	6.8	2.7
Lys	7.7	5	5.7	0.2	8.3	4	10.5	0.5
Phe	5.0	4	49.1	1.4	5.9	4	41.1	1.4
Arg	29.5	4	14.8	2.5	25.1	4	22.2	3.2
$CySO_3$	18.5	4	5.2	0.6	16.8	4	10.0	1.0
Pep*	28.2	4	15.9	2.6	33.1	4	11.7	2.2
εN-Lys	125	4	2.9	2.1	128	4	13.3	9.9

* Acid-resistant DNP-peptides.

tration is, however, revealed by the figures, although the expected difference is close to the experimental error. It should be noted at this stage that the N-terminal residues in the original untreated wool samples [3] represented a very small fraction of those found after tryptic digestion and it was not necessary to allow for them.

According to Table III the total number of α-DNP amino acids from a tryptic digest of normal wool was 330 μmoles/g. and 323 μmoles/g. from copper-deficient wool. By including the acid-resistant DNP-peptides, these figures might be raised to 360 μmoles/g., but this is far short of the 800 μmoles/g. expected from the arginine and lysine concentration. It is difficult to correct for losses during acid hydrolysis, but tests with pure DNP-amino acids suggested that hydrolysis for 11 hr. in the presence of undinitrophenylated digest, followed by the usual chromatographic or electrophoretic separation, caused a loss of about 40% of the DNP-cysteic acid; 30% of the DNP-arginine, di-DNP-lysine, DNP-threonine, and DNP-aspartic acid; 20% of the DNP-alanine and DNP-serine, and less of the others. Corrections of this magnitude might raise the total to 500 μmoles/g., which is still less than expected. Tryptic digestion for 16 hr. instead of 6 hr. increased the total by only about 6%, which was not confined to one or two amino acids, even when more enzyme was added after the first 8 hr., and, as already mentioned, there is doubt about whether this represents non-specific hydrolysis. It is therefore clear that a large proportion of the peptide bonds adjacent to lysine and/or arginine residues in oxidized wool is not affected by trypsin. Tests showed that this was also true of mohair, rabbit hair, and especially of human hair, which has a much higher cysteic-acid content than merino wool. The most probable explanation for this is that a large proportion of the arginine and lysine residues in wool and hair is associated with those of cysteic acid. It has been reported by Anfinsen and Redfield [1] that trypsin hydrolyzes the sequence arg. $CySO_3$ with difficulty. The presence of N-terminal cysteic acid in the tryptic digests of oxidized wool, however, suggests that not all sequences in wool containing cysteic-acid residues and a basic amino-acid residue are immune to trypsin.

Another unexpected feature of the results in Table III and previous tables is the relatively large amount of N-terminal lysine and arginine—about 55 μmoles/g. after correction. Some DNP-arginine might have been derived from free arginine liberated by the enzyme from double sequences such as arg. arg, but this cannot account for the lysine figures because no free di-DNP-lysine could be detected before acid hydrolysis. It is therefore probable that some of the basic amino-acid residues in oxidized wool are combined in sequences such as arg. arg. X, where the arg. X bond is not attacked by trypsin and X is presumably proline or cysteic acid [9].

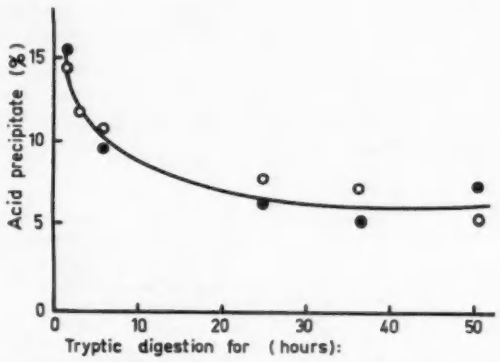

Fig. 3. Relation between amount of precipitate on acidifying a tryptic digest and the duration of digestion. Wool (E5): open circles—normal wool, full circles—copper-deficient wool.

Experiments on the Separation of Peptides from Whole-Wool Digests

The tryptic digests of oxidized wool were clear and light brown in color after the small amount of undigested residue had been centrifuged off. On acidifying the solution to pH 3.5 with acetic acid, a precipitate formed. Figure 3 shows that the amount of precipitate from oxidized normal and copper-deficient wool decreased with increasing duration of digestion. After dinitrophenylation, the precipitate from a 6-hr. digest of normal wool (E5) yielded about 70 μmoles/g. of mixed α-DNP-amino acids and 155 μmoles/g. of εN-DNP-lysine. The precipitate was therefore probably a mixture of high molecular weight peptides. According to Figure 3, prolonged tryptic digestion made this material more soluble and therefore more amenable to separation. This was considered more important than the possibility of a little non-specific hydrolysis, especially since the amounts of precipitate were similar in digests of the two sorts of wool, so tryptic digestion was continued for 24 hr. or more before attempting to separate the peptides.

The behavior of a 24-hr. tryptic digest of oxidized normal wool (E5) during paper electrophoresis at

pH 3.5 and 6.4 is shown in Figure 4. The approximate amounts of peptides in the various groups of bands are given as percentages estimated as described under "Methods." As expected, a large proportion of the peptides that were acidic at pH 6.4 moved towards the anode at pH 3.5.

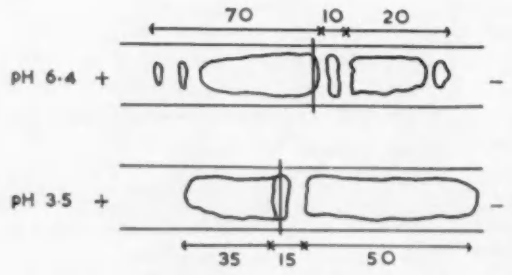

Fig. 4. Separation of peptides in a 24-hr. tryptic digest of oxidized normal wool (E5) by electrophoresis in pH 6.4 and pH 3.5 buffers for 8 hr. at 10 V/cm. The numbers are the approximate percentages of the total amount applied (2 mg.). The broad bands contained small bands of varying sharpness.

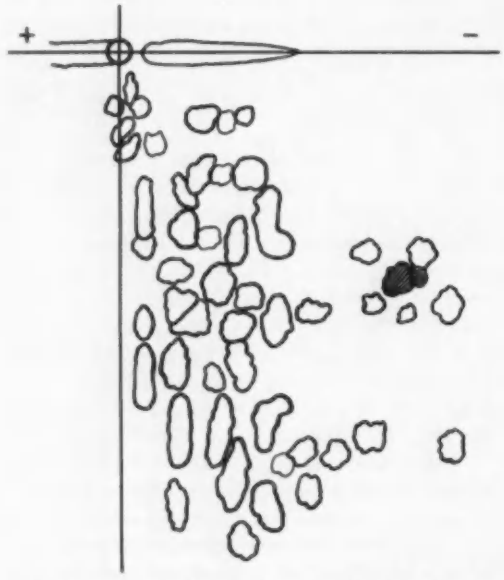

Fig. 5. Separation of peptides in a 24-hr. tryptic digest of oxidized wool (E5, normal) by electrophoresis at pH 3.5 (10 V/cm. 13 hr.) and chromatography using system A (descending, 16 hr.). The peptide mixture (5 mg.) was applied at the upper circle, which had a diameter of 2.5 cm.; the rest of pattern being in proportion. The shaded spots gave very intense colors with ninhydrin. The spots with thin edges were very faint and not always recognizable.

The separation of the same tryptic digest by paper electrophoresis at pH 3.5 followed by chromatography with system A is shown in Figure 5, which is an average pattern derived from several papers. The relative positions and intensities of the spots were reproducible if conditions were carefully standardized. Small changes in conditions were apt to give different patterns. It was not always easy to distinguish faint spots in the crowded regions of the paper. Some spots were differentiated by different shades of color or by their late appearance after ninhydrin treatment. No difference could be found between normal and copper-deficient wool in number, intensity, or positions of the spots.

Figure 6 shows the separation of the same tryptic digest of oxidized normal wool by electrophoresis at pH 6.4, followed by chromatography with system B. This pattern has also been constructed from several papers. The two most highly negative spots were usually allowed to run off the paper to improve the separation of the others. This system gives better separation of the negative peptides than that used for Figure 5, but is unsuitable for the basic and neutral peptides. Some overlapping of the neutral peptides between the two systems would be expected. A conspicuous feature of Figure 6 is the long negative spot which did not move during chromatography. This spot appeared to be shorter and less intense in digests of copper-deficient wool. No other difference between the normal and copper-deficient patterns was apparent.

A few preliminary tests were done on tryptic digests of other keratin fibers after oxidation. They included mohair, human hair, and other merino fibers. The electrophoretic and chromatographic pattern usually appeared to be similar to those given above, although insufficient tests have been done to be certain that there were no differences in detail. Human hair, however, was noticeable for a large increase in the size and intensity of the long negative spot referred to above.

The Separation of Peptides in Digests of Wool Fractions

A few tests were done on tryptic digests of the soluble and insoluble components of normal wool (E5) separated using pH 6 pyridine-acetate buffer as described in Part I [5]. The insoluble component was digested with trypsin in the same way as whole wool but the soluble component was first

isolated from solution by freeze-drying and then digested with a smaller amount of trypsin solution.

The electrophoretic and chromatographic behavior of digests of the insoluble component was very similar to that of whole wool digests. The pattern corresponding to Figure 5 was apparently identical, although that corresponding to Figure 6 showed that the insoluble component contained less of the peptide mixture responsible for the long negative spot, and some of the other spots appeared to be fainter.

The digests of the soluble component gave simpler patterns than the others. As expected from the high proportion of cysteic acid in this component, there appeared to be more negative and fewer positive peptides. The long negative spot in Figure 6 was much more prominent in patterns for which the same weight of soluble component had been used, and the two most negative spots were more intense. Most of the other negative spots appeared to be enhanced, although one group was apparently missing and there were a few faint new spots. The pattern corresponding to Figure 5 was much simpler for the soluble component, and it is shown in Figure 7. There are obviously fewer spots, and it is difficult to decide whether these correspond to any of those in Figure 5, apart from the very positive spot.

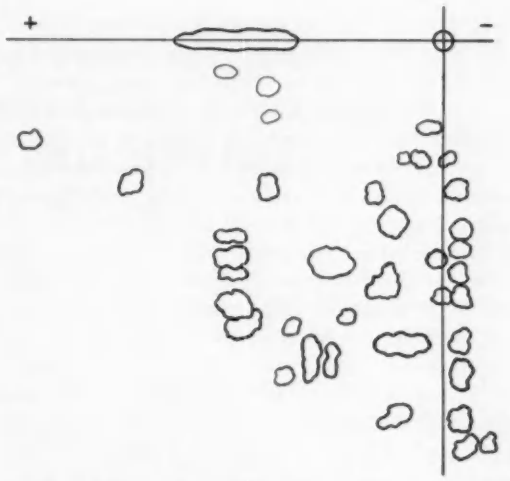

Fig. 6. Separation of peptides in a 24-hr. tryptic digest of oxidized wool (E5, normal) by electrophoresis at pH 6.4 (10 V/cm. for 14 hr.) and chromatography using system B (16 hr.). The two most negative spots are from an 8-hr. electrophoresis. The three small upper spots were clear in patterns for the soluble component, but faint in those of whole wool.

Other Attempts at Peptide Separation

Preliminary attempts were made at separating the peptide mixtures by ion-exchange chromatography. It was found that an acidic peptide fraction, about 40% by weight of the original wool, could be isolated from a tryptic digest of oxidized normal wool by the fact that it was not retained by an acidic (sulfonic) ion-exchange resin in the hydrogen form. This fraction included most of the soluble component and part of the insoluble component. It could be chromatographed on columns of DEAE-cellulose [16] by eluting with solutions of sodium acetate, as described in Part II [5], although using weaker solutions. Reproducible separations into discrete peaks and groups of peaks were obtained, in contrast to the behavior of the undigested soluble component. The acidic peptide fraction from the tryptic digests of the insoluble component was separated into 7 groups of peaks in this way.

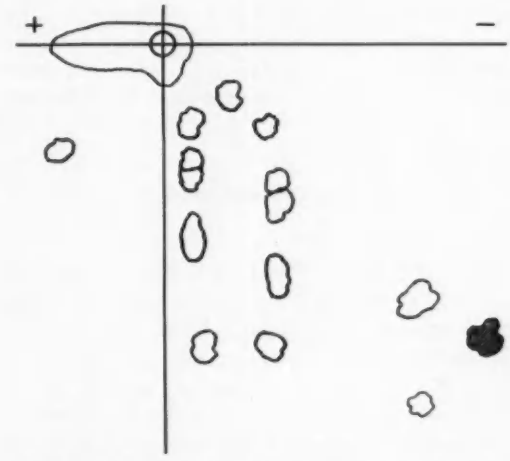

Fig. 7. Separation of peptides from a 25-hr. tryptic digest of the soluble component from oxidized wool (E5, normal) by electrophoresis at pH 3.5 and chromatography with system A, under the same conditions as for Figure 5. Five milligrams was applied. The shaded spot probably corresponded to one of those shaded in Figure 5.

Discussion

The above results show that, apart from a small difference in the proportions of a group of negative peptides separated by paper electrophoresis and chromatography, the tryptic digests of oxidized normal and copper-deficient wool contain a similar mixture of peptides. It need hardly be emphasized that the methods of analysis and separation used were

very crude; they were applied in the hope of revealing any large differences in the arrangement of the amino-acid residues in the two sorts of wool.

The N-terminal-residue estimations showed that oxidized wool keratin is incompletely hydrolyzed by trypsin, about a third of the possible sites remaining unhydrolyzed. Such resistance to trypsin is unusual and it limits the usefulness of methods such as those described here. The reasons for this and the distribution of the immune sites have not been investigated. It is possible that a third of the basic amino-acid residues are adjacent to proline, because arg. pro sequences, for example, appear to be resistant to trypsin [9]; but it is more likely that the most characteristic feature of oxidized wool, namely, its high concentration of cysteic-acid residues, is responsible [1]. If this is true it suggests that a convenient method of getting sequence information about the sulfur-rich regions of wool, which is particularly important for a complete understanding of its properties, would be to digest the oxidized wool or wool fractions with trypsin and then examine the high molecular weight peptides. Some preliminary experiments on the isolation and separation of the acidic peptides have been carried out and a continuation of these investigations may lead to a better understanding of the relation between the sulfur-rich and sulfur-poor regions of the original fibers.

Acknowledgments

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Effect of Elongation and Temperature on the Recovery and Apparent Glass Transition Behavior of an Experimental Modacrylic Fiber[1]

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Abstract

The shape of the stress–strain curve of the modacrylic fiber is correlated in a definite manner with the stress-relaxation and recovery behavior. At the yield point, where the stress–strain curve has minimum slope, the tensile recovery decreases most rapidly with increasing elongation, and the rate of stress relaxation passes through a maximum. Above the normal (low-strain) glass transition temperature of the fiber (90° C.), the stress–strain curve no longer has a yield point, and the recovery and stress-relaxation behavior become relatively independent of elongation.

The tensile- and work-recovery values show a definite minimum (permanent set shows a maximum), occurring at the glass transition temperature at low, 1%, strain, and shifting to lower temperatures with increasing elongation. This shifting of the minimum in the recovery–temperature curves is interpreted to indicate a lowering of the glass transition temperature with stretching. At temperatures of 25° and 60° C., the yield strain approximates that elongation required to reduce the minimum in the recovery–temperature curves to that temperature. These results lead to a fundamental definition of the yield point as the strain level at which the glass transition temperature is lowered to the experimental temperature.

A free volume increase accompanying stretching is postulated as the underlying mechanism whereby the glass transition temperature is reduced. The equations of Ferry [13, 14] indicate that a quite reasonable value of 0.35 for Poisson's ratio could lead to an increase in free volume sufficient to speed up the molecular response by a factor of 10^5 at the yield strain.

Introduction

The ability to recover from deformation is one of the most important functional properties which a successful textile fiber must possess, and considerable attention has been devoted in the literature to the measurement of this property. Previous investigations of fiber tensile recovery have been of two general types. Either recovery from a range of elongations has been studied at standard conditions [1, 2, 3], or the recovery from a constant low elongation has been studied over a range of temperatures [4, 5]. Whereas the recovery under standard conditions from various elongations is more useful in estimating fiber and fabric performance under the test conditions, the high temperature stiffness and recovery from low strains have indicated the important changes in fiber behavior which occur at the glass transition temperature, T_g. The most notable changes are a drop in stiffness and minimum in recovery which occur over the temperature range near T_g. Measurements on wet fibers have shown that water plasticizes most fibers and lowers T_g to an extent dependent on the water sorption of the fiber [5].

The present paper combines the two earlier approaches by extending recovery–temperature measurements to include a range of elongations up to 10%. Measurements of stress, stress relaxation, and recovery as a function of elongation are also presented and correlated at several temperatures. From a consideration of all of these results, a new

[1] Paper presented at the Fall meeting of The Fiber Society in Washington, D. C., October 28, 1960.

interpretation of the stress–strain curve is postulated, based on a lowering of the glass transition temperature of the fiber as stretching occurs.

Except where otherwise noted, the results of the present paper were obtained on an experimental modacrylic fiber containing 70% acrylonitrile. As shown in Figure 1, the recovery–temperature curve of this fiber, measured at low, 1%, elongation, shows a minimum near 90° C. which is nearly independent of molecular orientation. Other acrylic and modacrylic fibers also show low-strain recovery minima near 90° C. [4, 5]. Figure 2 compares volume–temperature and recovery–temperature data on Dynel (40/60 acrylonitrile/vinyl chloride copolymer), and shows that the recovery minimum measured at low strains occurs at the dilatometric glass transition temperature of the polymer. The fact that the dilatometric measurements were made on a molded bar, whereas oriented fibers were employed in the recovery measurements, is a further indication that T_g for acrylics is not very dependent on molecular orientation. In view of distinct similarities in stress–strain characteristics, as well as in transition behavior already cited, it is believed that the results obtained on the experimental modacrylic fiber will be at least qualitatively applicable to other acrylic and modacrylic fibers.

Experimental Methods

All measurements were carried out in a room maintained at 76° F. and 50% relative humidity. Recovery–temperature measurements were made using an electrically heated furnace mounted in an Instron tensile tester as described by Brown [4]. Two-inch specimens of continuous filament yarn were employed and stretched at 0.2 in./min. A new specimen was employed for each measurement, since stretching to elongations beyond the yield region substantially influences the subsequent viscoelastic behavior of the fiber.

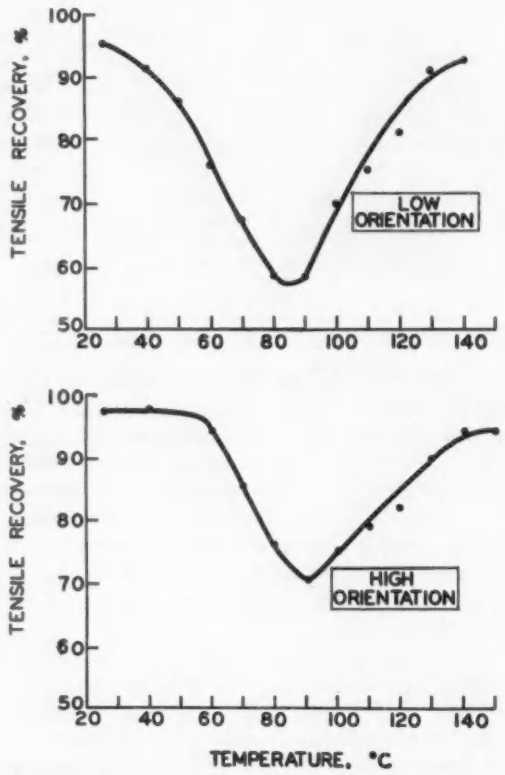

Fig. 1. Recovery–temperature behavior at 1% elongation for experimental modacrylic fibers of high (normal) and low orientation.

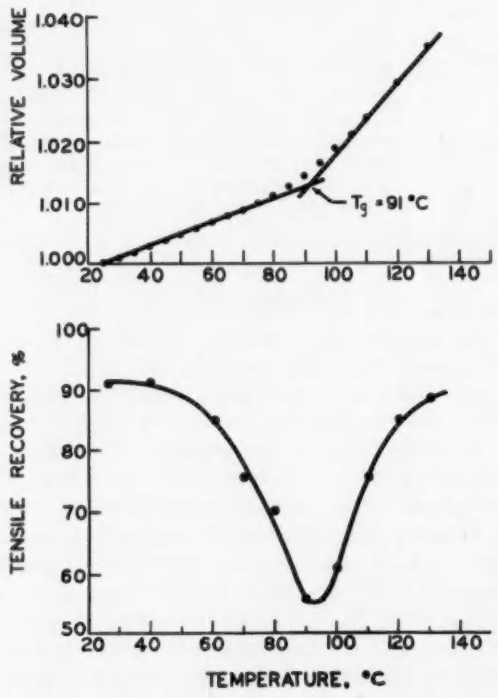

Fig. 2. Volume–temperature and recovery–temperature behavior of Dynel. Recovery–temperature curve measured at 1% elongation.

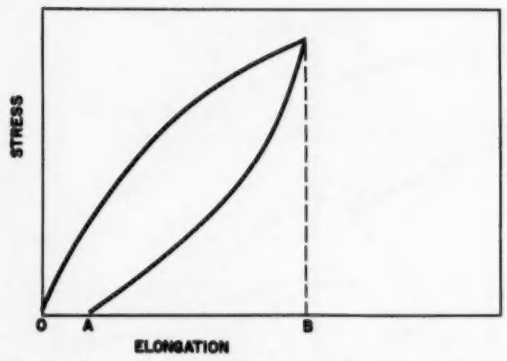

Fig. 3. Simple stretch cycle for measuring tensile recovery.

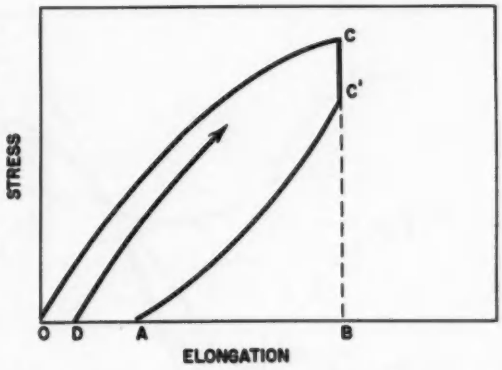

Fig. 4. Stretch cycle for measuring work recovery, stress relaxation, and "permanent" set.

In the first stage of the investigation, the tensile recovery was measured at temperatures up to 180° C.; tensile recovery was defined as (AB/OB) × 100 according to the diagram in Figure 3. In these initial experiments, the yarn was tested in the "as received" state, and shrinkage of the specimens was found to occur at temperatures of 100° C. or greater. The shrinkage was practically linear with temperature above 100° C., and amounted to approximately 8% at 180° C.

In later experiments, specimens were annealed untensioned for 3 min. at 160° C. prior to testing, in order to eliminate shrinkage as a variable between specimens tested at different temperatures. The highest temperature employed in this second series of tests was 120° C.; the stretching procedure was changed as shown in Figure 4 to include a stress-relaxation interval CC' of 60 sec., and a measure of percent "permanent" set, (OD/OB) × 100, 5 min. after completion of the first stretching cycle. This procedure is similar to that employed by Beste and Hoffman [2]. Work recovery was measured in this second set of experiments from the ratio of areas under the extension and retraction portions of the cyclic stress–strain curves, using an Instron Integrator with appropriate corrections applied [6].

Results and Discussion

Effect of Temperature and Elongation on Recovery

Figure 5 shows the results of duplicate measurements of the tensile recovery (defined according to the procedure of Figure 1), plotted as a function of temperature for elongations of 1%, 3%, 5%, and 10%. The 1% elongation curve shows a minimum near 90° C., which characterizes the glass transition temperature of the fiber. At 3% elongation, the recovery minimum is deeper and occurs at a lower temperature, about 65° C. At elongations of 5% and 10%, the minimum in the recovery curve is quite broad and extends through the room temperature region. At the highest strain level of 10%, a second minimum in the recovery–temperature curve is suggested by the data at the higher temperatures. The significance of this second minimum is not understood, and subsequent measurements were limited to temperatures of 120° C. or less.

The recovery–temperature measurements were repeated using annealed specimens and the stretching procedure illustrated in Figure 4. The work-recovery results are shown as a function of temperature in Figure 6 for elongations of 1%, 2%, 5%, and 10%, and the corresponding permanent set–temperature curves are shown in Figure 7. Each point in these two graphs represents an average of three determinations, which usually fell within ± 2% of the average. These results also indicate a broadening and shifting of the minimum recovery region to lower temperature as the elongation is increased. The shifting of the curves to lower temperatures at the 2% strain level is more evident in Figure 7, which shows the characteristic maximum in the permanent set curve shifting from about 85° C. for 1% stretch to near 60° C. for 2% stretch. At the higher strain levels of 5% and 10%, both the work-recovery and permanent-set curves become quite attenuated so that the minimum or maximum regions extend below room temperature.

Since the recovery minimum has been shown to be characteristic of the glass transition temperature

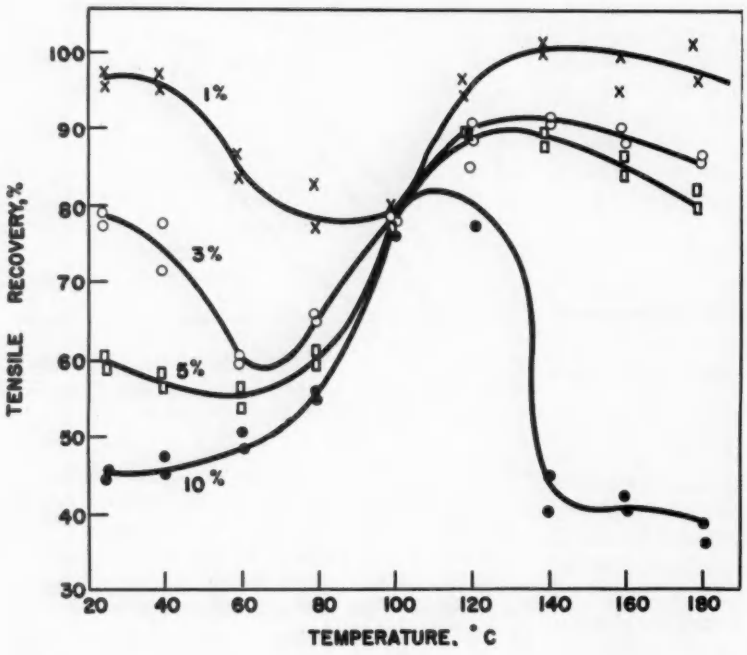

Fig. 5. Tensile recovery from various elongations as a function of temperature; experimental modacrylic fiber.

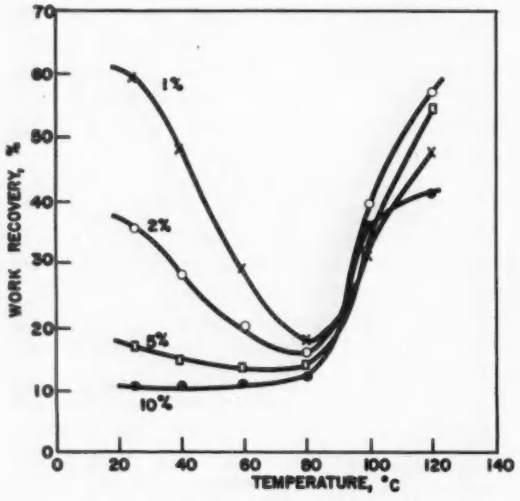

Fig. 6. Work recovery from various elongations as a function of temperature; experimental modacrylic fiber.

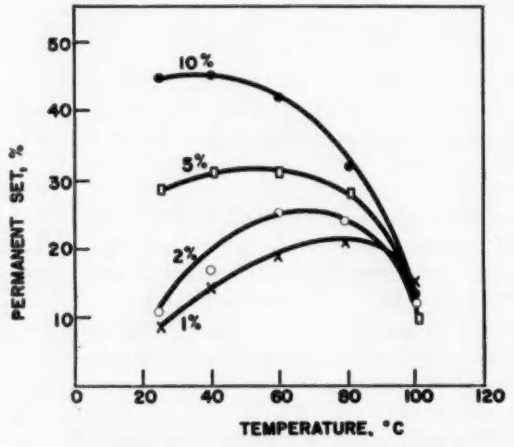

Fig. 7. Permanent (5-min.) set at various elongations as a function of temperature; experimental modacrylic fiber.

of a polymer, the systematic change in the recovery–temperature behavior with elongation suggests that increasing strain (or stress) acts to lower the glass transition temperature of the fiber. The broadening of the minimum in the recovery–temperature curves may be attributed to the longer times during which the specimens are under load at the higher elongations, and to the likelihood that the lowering of T_g with increasing elongation is not uniform for all viscoelastic elements in the fiber.

An interesting common feature of Figures 5–7 is the fact that the percent recovery becomes very

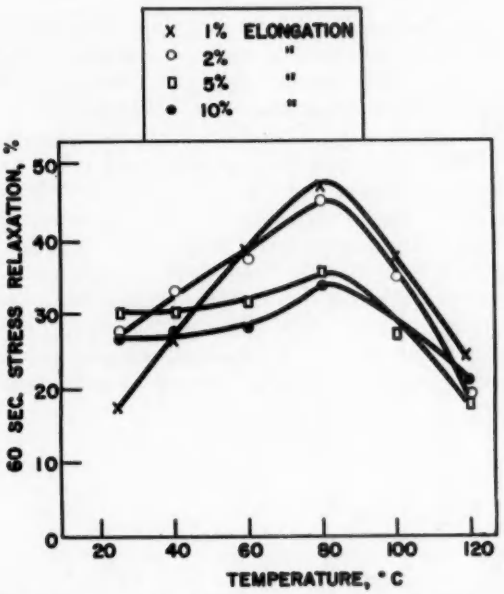

Fig. 8. Stress relaxation at various elongations as a function of temperature; experimental modacrylic fiber.

nearly independent of elongation at 90–100° C., i.e., just above the glass transition temperature of the unstrained fiber. At still higher temperatures, the recovery behavior again becomes quite strain-dependent, as shown in Figure 5.

Effect of Temperature and Elongation on Stress Relaxation

60-Second stress-relaxation curves were recorded while measuring recovery behavior by the stretching procedure illustrated in Figure 4. Figure 8 shows the fraction of the original stress which decayed in 60 sec. over a range of temperatures at elongations of 1%, 2%, 5%, and 10%. Each point shown represents the average of three measurements. At the lower elongations, the rate of stress relaxation passes through a maximum near the glass transition temperature, as noted by Brown [4]. At higher elongations, the relaxation rate curve becomes flatter in the temperature interval between 25° and 60° C., and the maximum near 80° C. becomes less pronounced. The systematic shifting of the apparent transition temperature with elongation which was found in the recovery curves is not present in the relaxation–temperature curves; however there is a broadening of the curves at higher elongations which suggests an attenuation toward the lower

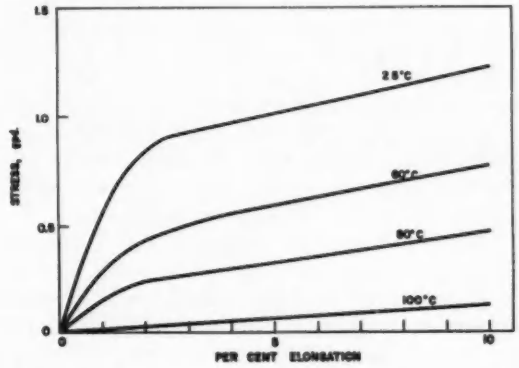

Fig. 9. Stress–strain curves of experimental modacrylic fiber at various temperatures.

temperature side at the higher elongations. As in the case of the recovery and permanent-set curves, the stress-relaxation behavior becomes relatively—though not entirely—independent of elongation above T_g, in this case between 100° and 120° C.

A constant rate of elongation was employed in stretching the fibers prior to the stress-relaxation measurement, so that more relaxation occurs during stretching to the higher elongations. Holding the stretching time constant would probably change the relaxation–temperature curves significantly. The effect of stretching time on the stress-relaxation behavior at room temperature is examined in the section below.

Relation Between Stress–Strain, Recovery, and Stress-Relaxation Behavior

Several instances have been cited where the viscoelastic behavior becomes essentially independent of elongation near 100° C. Figure 9 shows the stress–strain behavior up to 10% elongation at temperatures of 25°, 60°, 80°, and 100° C., from which it can be seen that the "knee" or yield region of the stress–strain curve disappears near 100° C. This feature suggests that a correlation exists between the shape of the stress–strain curve and viscoelastic behavior such as recovery and stress relaxation. This correlation is examined at room temperature for the experimental modacrylic fiber in Figure 10.

Figure 10 shows the stress–strain (curve A) and recovery–elongation (curve B) relationships for unannealed specimens of the experimental acrylic fiber at room temperature. The recovery values were measured according to the procedure of Figure 3. It can be seen that as the slope of the stress–strain curve

decreases, the rate at which the recovery drops off with increasing elongation starts to increase. At the yield region near 3% or 4% elongation, where the stress–strain curve has minimum slope, the recovery is falling most rapidly with increasing elongation. At post-yield elongations where the fiber starts to stiffen, the recovery drops off more slowly, until at the highest elongations it has nearly leveled off.

The stress-relaxation behavior (curve C, Figure 10) also correlates with the stress–strain and recovery behavior. In this case the fiber was stretched at a rate of 100%/min. to reduce somewhat the stress relaxation which occurred during stretching. The stress-relaxation rate measured over the first 5 min. increases with increasing elongation, passing through a maximum at the yield elongation, and subsequently decreasing slightly in the post-yield region. The stress relaxation vs. elongation curve is thus related to the slope of the stress–strain curve.

Figure 11 compares the 5-min. stress relaxation vs. elongation curve of Figure 10 with that obtained when the rate of stretching was varied so as to hold the stretching time constant at $0.2 \pm .02$ min. Thus at 20% elongation the two sets of curves come together. Although the maximum in the relaxation rate is less pronounced when the stretching times were held constant, the essential features of the curves remain unchanged. Figure 11 also shows

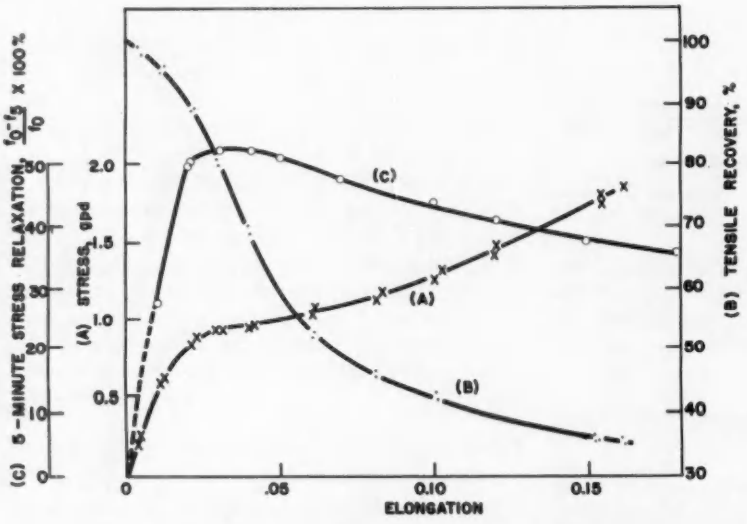

Fig. 10. Stress (A), tensile recovery (B), and stress relaxation (C) as a function of elongation at room temperature. Experimental modacrylic fiber.

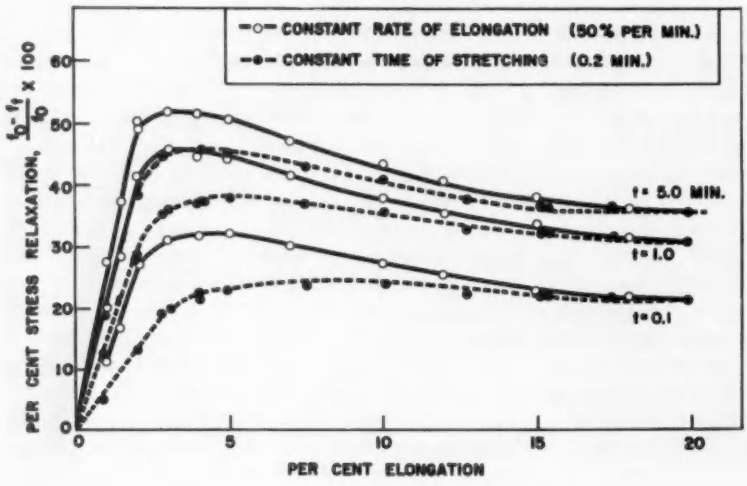
CONSTANT RATE OF ELONGATION (50% PER MIN.)
CONSTANT TIME OF STRETCHING (0.2 MIN.)
PER CENT STRESS RELAXATION, $\frac{f_0 - f_f}{f_0} \times 100$
PER CENT ELONGATION
t = 5.0 MIN.
t = 1.0
t = 0.1

Fig. 11. Stress relaxation as a function of elongation for variable and constant stretching times; experimental modacrylic fiber.

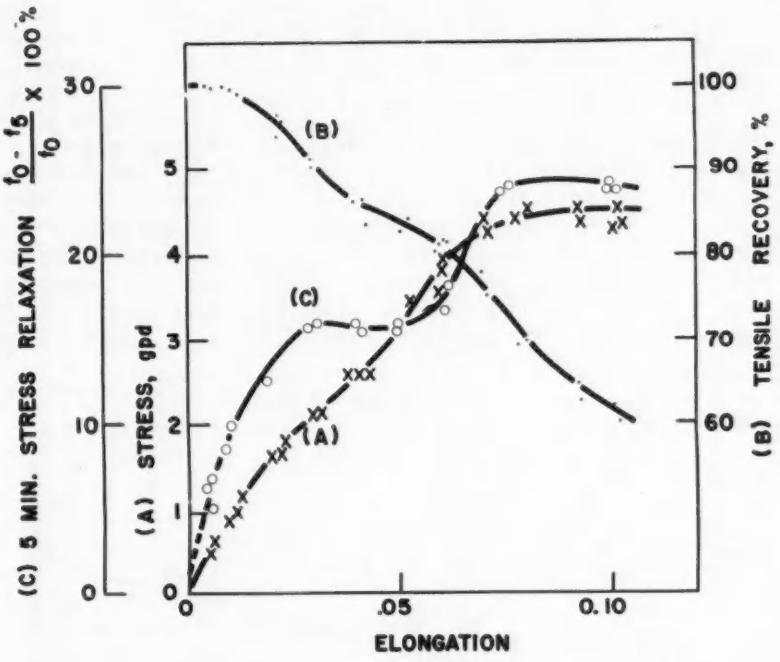

Fig. 12. Stress (A), tensile recovery (B), and stress relaxation (C) as a function of elongation at room temperature. Polyethylene terephthalate polyester fiber.

the relaxation rate measured over shorter time intervals of 1.0 and 0.1 min.; it can be seen that the elongation of maximum relaxation rate increases at shorter times. This corresponds with an increase of apparent yield strain with increasing rate of elongation, which does occur.

Figure 12 shows the recovery, stress-relaxation and stress–strain behavior of a polyethylene terephthalate filament yarn at room temperature. The stress–strain curve of the polyester differs markedly from that of the modacrylic fiber, and shows two apparent yield regions. At the first yield region near 3% elongation, the recovery curve falls off rapidly, but starts to level off slightly in the post-yield region of 4–6% elongation where the fiber becomes stiffer. The recovery again falls off rapidly in the second yield region above 7% elongation. The stress-relaxation behavior of the polyester fiber (curve C, Figure 12) also reflects the features of the stress–strain curve. At the first yield region, the rate of stress relaxation passes through a maximum. Beyond this point the relaxation rate decreases slightly and then increases in the second yield region above 7% elongation. As in the case of the modacrylic fiber, a definite correlation exists between the characteristic features of the relaxation, recovery, and stress–strain curves.

Figures 13, 14, and 15 show similar three-ordinate plots for the experimental modacrylic fiber at several elevated temperatures. At 60° C. (Figure 13), the stress–strain curve, labeled A, shows a yield region near 2% elongation, a somewhat lower yield strain than observed at room temperature. The recovery curve, B, appears to have a slight inflection in the yield region, and the rate of relaxation curve, C, passes through a well defined maximum.

The data measured at 100° C. and plotted in Figure 14 show that the stress–strain curve no longer has a yield region at that temperature. The relaxation rate data, labeled C, show no maximum such as was found at lower temperatures. Recovery data, plotted as solid circles, show considerable scatter, probably due to temperature fluctuations plus the fact that recovery is a sensitive function of temperature near 100° C. The possible maximum indicated in curve B cannot be explained, and is of doubtful validity in view of the scatter.

Data at 120° C. are shown in Figure 15. At this temperature the stress–strain curve A is almost linear and shows no yield point; the recovery curve B is

practically flat; and the rate of relaxation data show considerable scatter but are probably best represented by a horizontal line.

Interpretation of the Stress–Strain Curve

The recovery–temperature curves presented in Figures 5–7 show a distinct minimum in recovery (or maximum in permanent set) from 1% stretch, which occurs at the glass transition temperature of the fiber. At higher elongations, the temperature at the recovery minimum (or permanent set maximum) is decreased, reaching 60–65° C. for elongations of 2% or 3%. For elongations of about 5% or greater, the minimum in the recovery curve becomes very broad and extends through the room temperature region. This shift in the recovery–temperature curves is interpreted as indicating a lowering of the glass transition temperature with increasing strain.

The yield point in the stress–strain curve at room temperature was found to occur between 3% and 4% elongation—close to the same elongation where the minimum in the recovery–temperature curve first spans room temperature. Also, the yield point found at 60° C. was near 2% elongation, which is near the T_g indicated for that elongation by Figure 7.

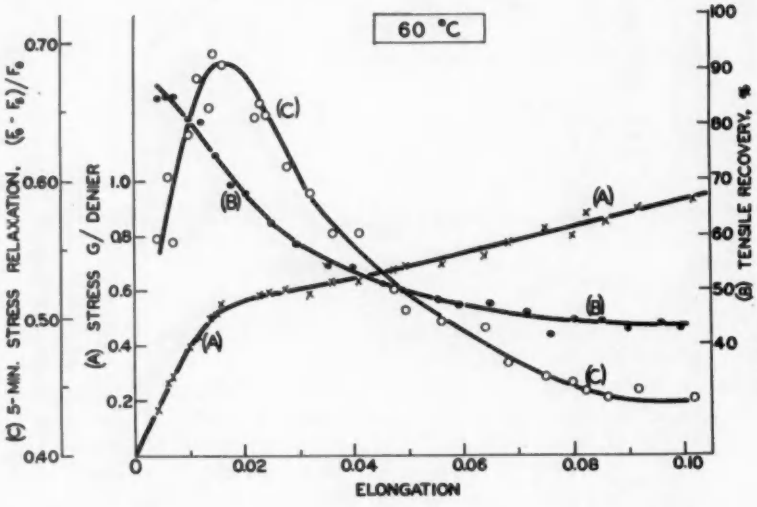

Fig. 13. Stress (A), tensile recovery (B), and stress relaxation (C) as a function of elongation at 60° C. Experimental modacrylic fiber.

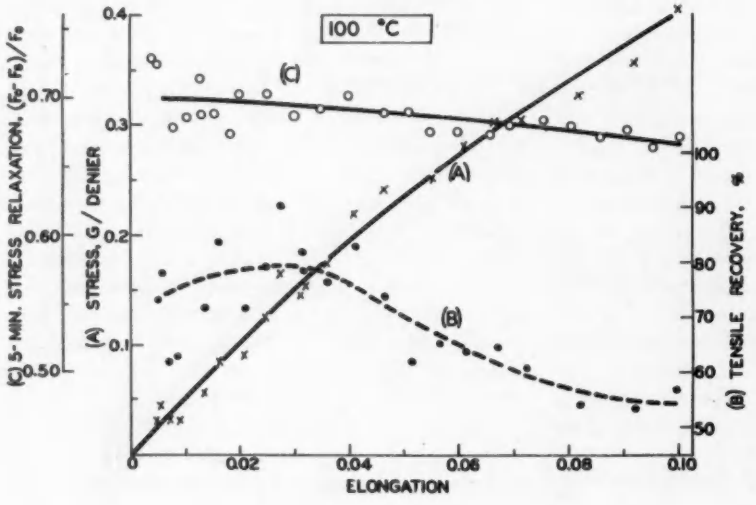

Fig. 14. Stress (A), tensile recovery (B), and stress relaxation (C) as a function of elongation at 100° C. Experimental modacrylic fiber.

Above the dilatometric T_g, the stress–strain curve no longer shows a yield point. Therefore the postulate is made that *the yield point occurs at that elongation which reduces* T_g *to the temperature of testing*. As the experimental temperature is increased, the yield strain, i.e., the strain required to lower T_g to the test temperature, is decreased. On this basis, the absence of a yield point in the stress–strain curves of wet nylon [7] and wet viscose rayon can be attributed to the fact that T_g is below room temperature due to the plasticizing effect of water [5]. The fact that the rate of stress relaxation is a maximum at the yield point, just as it is at T_g, is a further indication of similar behavior found at T_g and the yield point. Like all effects associated with the glass transition, the exact location of the yield point would be expected to be quite dependent on the rate of testing, as observed.

Meredith [7] has interpreted fiber stress–strain curves in terms of a transition from glassy to rubbery behavior at the yield point, such as that for which evidence is presented here. Riley and Carolan [8] have also given a somewhat similar interpretation of the stress–strain behavior of cellulose acetate. The latter authors postulated melting of certain regions of the fiber due to superheating as the cause of the low post-yield stiffness in acetate.

The glass transition point can be considered as that temperature at which the average response time for the molecular segments of a polymer becomes equal to the time interval of the experiment [4]. Therefore the postulated lowering of T_g with increasing strain is equivalent to saying that the molecular response processes of the fiber become faster at higher strains. This viewpoint is supported by the results of Passaglia and Koppehele [9] on the stress relaxation of viscose rayon monofilaments, which indicated that an increase in strain level was equivalent to an increase in time. The results of Catsiff, Alfrey, and O'Shaughnessy [10] on the creep behavior of nylon also showed an equivalence between stress (and hence strain) and time. Such results are analagous to the well-known equivalence between time and temperature, which has been demonstrated on numerous polymer systems above T_g by Ferry [11] and Tobolsky [12].

Mechanism for Lowering T_g *by Stretching*

The mechanism by which T_g may be lowered by stretching has been suggested in the recent work of Ferry [13, 14], which has shown that the glass transition temperature for a wide variety of polymers and glass-forming liquids represents an iso free volume point, at which the fractional free volume is approximately 0.025. The change in fractional volume which accompanies stretching to an elongation ϵ is given by the following expression [15]:

$$\Delta V/V = (1 - 2\mu)\epsilon \qquad (1)$$

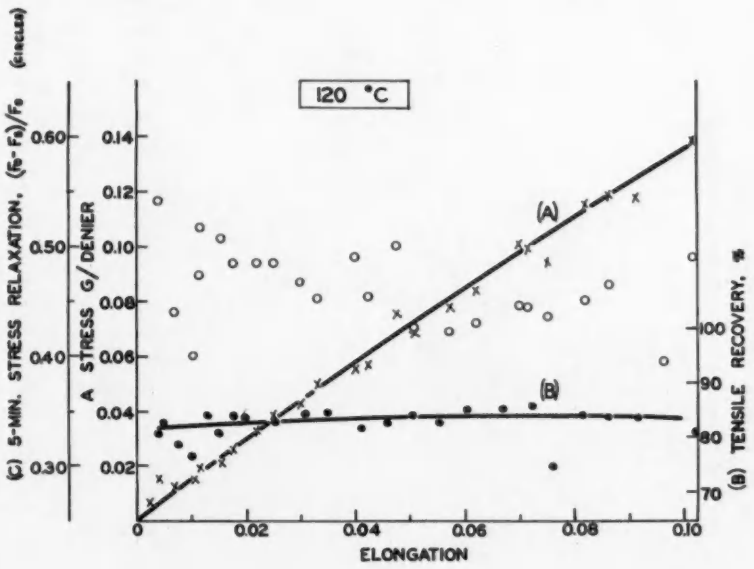

Fig. 15. Stress (A), tensile recovery (B), and stress relaxation (C) as a function of elongation at 120° C. Experimental modacrylic fiber.

where μ = Poisson's ratio. No data are available regarding Poisson's ratio for the experimental modacrylic or other acrylic fibers. However a value of 0.38 has been measured for nylon 66 [16], and values of 0.35 ± 0.02 and 0.34 have been reported for unoriented samples of polymethylmethacrylate [17] and polystyrene [18], respectively. For a value of 0.35 for μ, the relative volume increase, $\Delta V/V$, calculated from Equation 1 equals 0.015 for an elongation of 5%.

The effect which such a volume increase may have on the response time of a polymer can be estimated from the following equation, which has been derived by Williams, Landel, and Ferry [13] from the viscosity equation of Doolittle [19]:

$$\log \frac{\tau_{st.}}{\tau_{unst.}} = (1/2.303)(1/f_{st.} - 1/f_{unst.}) \qquad (2)$$

where $\tau_{st.}$ and $\tau_{unst.}$ are the relaxation times of any given viscoelastic element in the stretched and unstretched states, $f_{st.}$ is the fractional free volume in the stretched state, and $f_{unst.}$ the fractional free volume in the unstretched state.

For stretching carried out below T_g, $f_{unst.}$ will have a value near 0.025. An upper limit for $f_{st.}$ can be estimated by assuming that all of the volume change from Equation 1 represents a change in free volume. This assumption has not been verified, although the work of Doolittle [19] has verified the equivalent assumption for volume changes resulting from temperature changes (rather than due to tensile elongation or internal pressure changes as in the present case). Substituting the value of $0.025 + 0.015 = 0.040$ for the value of $f_{st.}$ in Equation 2 gives a value of -6.5 for the logarithmic shift factor $\log (\tau_{st.}/\tau_{unst.})$. Thus, strains of the order of the observed yield strain at room temperature, 3–4%, could be expected to speed the molecular response by a factor of 10^4 to 10^5, which could well carry the fiber into a rubber-like response. The present interpretation leads to the prediction that for strains beyond the yield region, Poisson's ratio will increase and approach the value of 0.5 exhibited by most rubbery solids.

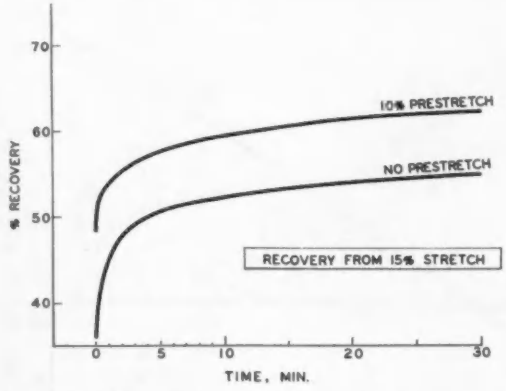

Fig. 16. Influence of prestretch on subsequent recovery from 15% elongation.

Although experimental evidence for a lowering of T_g with stretching is available only for the experimental modacrylic fiber, the interrelationships between the recovery, stress-relaxation, and stress–strain curves noted in Figure 12 suggest that the same principles may be valid for polyethylene terephthalate, and possibly other fibers and polymers. The data of Davis [16] show definite similarities between the volume–strain behavior of Terylene, and the stress–strain and relaxation–strain curves of Figure 12.

Influence of Pre-Stretch on Recovery Behavior

Figure 16 shows results of a test designed to detect the acceleration of molecular response under strain which has been postulated above. The experimental modacrylic yarn was stretched 15% and released, and its recovery measured over an extended period of time as shown in the lower curve in Figure 16. A second specimen was stretched 10% and allowed to recover for 90 min., after which a second stretch of 15% was superimposed. A previously determined recovery vs. time relationship for a single 10% stretch was used as the base line for calculating the percent elongation and recovery for the second stretch of 15%, so that the curves for the first and second stretches would coincide if the principle of superposition of strains were to hold. The substantially higher recovery for the second stretch (curve labeled "10% prestretch") indicates that the superposition principle does not hold; the higher recovery is believed to be due to the acceleration of the first recovery by the second stretch.

Summary and Conclusions

The following observations have been made for the experimental modacrylic fiber under study:

1. The minimum in the low-strain recovery vs. temperature curve, which is characteristic of the

glass transition temperature region, is broadened and shifted to lower temperatures when the fiber is stretched to higher elongations. Between 3% and 5% elongation (the yield region of the stress–strain curve at room temperature), the minimum in the recovery–temperature curve becomes quite broad and spans room temperature. At or just above the glass transition temperature of the unstrained fiber, the recovery behavior becomes independent of elongation; this corresponds to the temperature where the initial stiff portion of the stress–strain curve first disappears. At still higher temperatures, recovery again becomes elongation-dependent.

2. The initial rate of stress relaxation passes through a maximum at the glass transition temperature. The relaxation rate vs. temperature curves become attenuated toward lower temperatures with increasing elongation, but do not show a discernible shift in the temperature of maximum rate analogous to the shift of the recovery vs. temperature curves. It may be significant that of all of the viscoelastic measurements which were made, stress relaxation is the only one which does not allow any deformation of the test specimen to occur during the experiment.

3. Measurements of the stress, recovery, and stress relaxation as a function of elongation show that these quantities are correlated in a definite manner. The rate of stress relaxation passes through a maximum in the yield region of the stress–strain curve where the recovery–elongation curve is falling most rapidly. The yield elongation at a given temperature corresponds approximately to the strain level at which the minimum in the recovery–temperature occurs at the particular temperature.

Based on these observations, a decrease in the glass transition temperature of the fiber with increasing elongation is postulated. The yield point then corresponds to the elongation region at which the glass transition temperature is reduced to the experimental temperature. The postulated reduction of T_g with elongation is believed to result from an increase in free volume which occurs. With reasonable assumptions for Poisson's ratio, it can be estimated from the equation of Williams, Landel, and Ferry [13] that the speed of molecular response in the fiber may be increased by a factor as great as 10^6 at an elongation of 5%.

Acknowledgment

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The Efficiency of Multiple Spindle Automatic Winding Machines with Constant Patrolling and Servicing Times

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Abstract

A general solution for the efficiency of a single winding spindle is given, where the patrolling time of the automatic knotting unit may be less than the unwinding time of the supply bobbin. Constant supply bobbin unwinding times and random yarn breaks are assumed in obtaining the solution, which is modified to allow for "doffing" and servicing times.

The case where different winding spindles are allocated to supply bobbins having different unwinding times is considered, and the patrolling time giving the maximum combined spindle efficiency is determined by means of a simple arithmetic technique.

1. Introduction

1.1 *Essential Machine Features*

On certain well-known automatic winding machines used to wind yarn from a relatively small supply bobbin (usually a ring bobbin) onto a large cheese or cone, a number of spindles forms a self-contained machine (between about 90 and 360 spindles). An automatic knotting unit patrols the machine in a fixed time and spends a fixed time servicing each spindle, i.e., replacing an exhausted supply bobbin by a full one and starting it, or knotting a thread which has broken and re-starting it. All the unwinding is done at the same linear yarn speed so that we may speak of the "length of yarn" on the bobbin and the "unwinding time" of the bobbin (i.e., the time required to unwind it completely in the absence of breaks) as equivalent. The supply bobbins on two different spindles do not necessarily contain the same length of yarn, but all the bobbins unwound on the same spindle have the same nominal unwinding times. The patrolling time, i.e., the time between consecutive arrivals of the knotting unit at a particular spindle, can be varied within certain limits, and is set at the value which will give maximum efficiency, i.e., the highest possible ratio of time spent on actual unwinding to total running time of the machine.

On earlier models of this type of machine the arrival of the unit at a spindle which was running stopped the spindle, so that maximum efficiency was attained by making the patrolling time exceed by as little as possible the unwinding time of the largest supply bobbin on the machine, since the amount of time lost as a result of yarn breaks is a minimum when the patrolling time has its smallest possible value. On later models,[1] however, a spindle continues to run in spite of the arrival of the knotting unit, so that patrolling times smaller than the unwinding times of some or all of the supply bobbins on the machine can be used. The "servicing time," i.e., the time spent by the unit at each spindle, is the same whether the spindle is stopped or running, so that the patrolling time is strictly constant. With such machines the problem of finding the patrolling time which will give the maximum efficiency is more complicated.

It is convenient to consider separately two cases: the case in which there is only one spindle on the

[1] For example Model D Spooler, Barber-Colman Company, Rockford, Illinois; Model 202 Automatic Cone Winder, Foster Machine Company, Westfield, Massachusetts.

machine or there are more than one but all supply bobbins have the same unwinding time; the case in which supply bobbins with different unwinding times are being simultaneously unwound on different spindles of the machine. The present paper discusses both these cases, in Sections 2 and 3 respectively. In both cases random breaks are first ignored and later taken into account. The case in which there is a single spindle and random breaks are taken into account has been discussed mathematically by Howie and Shenton [1], and their result is the foundation of the solution obtained here.

In practice, when a supply bobbin has had a yarn break it is not usually knotted and immediately unwound on the same spindle; it is frequently removed and replaced by another supply bobbin, its unwinding being later completed on the same or another spindle. It is clear that in the long run the order in time in which the bobbins are unwound has no effect on the efficiency of the process.

1.2 *Assumptions Made in Arriving at the Solution*

(i) *Random breaks.* (a) In examining the effect of random breaks it is assumed that within each supply bobbin breaks occur independently and with uniform probability throughout the length of the bobbin, i.e., a break is as likely to occur at any one position in the bobbin as at any other. This assumption has two consequences: (i) the *average* number of breaks in a bobbin is proportional to its "unwinding time" (in the sense defined in paragraph 1.1), i.e., if a bobbin has unwinding time l, the number of breaks in it has average value μl, where μ is a positive constant and is in fact the average number of breaks in a bobbin of unit length (or unwinding time); (ii) in a bobbin of unwinding time l (and average number of breaks μl) the probabilities of 0, 1, 2, 3, . . . breaks are given by Poisson's distribution, i.e., they are

$$e^{-\mu l}, \quad (\mu l)e^{-\mu l}, \quad (\mu l)^2 e^{-\mu l}/2!, \quad (\mu l)^3 e^{-\mu l}/3! \ldots$$

respectively.[2] While detailed information on the distribution of yarn breaks during unwinding from different types of bobbin is scanty, the authors have found the above assumption to be valid when cotton yarn is unwinding from parallel wound ring bobbins. Other confirmation of the validity of the assumption in particular instances is available [2].

(b) When random breaks are taken into account the number of patrols required to unwind completely a bobbin of length l is itself a random variable: let its average value be $\bar{N}$. If T is the patrolling time, the average time required to unwind this bobbin is $\bar{N}T$, so that the average efficiency is

$$\bar{E} = l/\bar{N}T \tag{1}$$

The problem of calculating $\bar{E}$ therefore reduces to that of finding $\bar{N}$.

(ii) *Bobbin unwinding time.* The unwinding times of similar supply bobbins unwound on the same spindle have been assumed to be constant. In practice there is a certain small amount of variation in the length of yarn wound on nominally similar ring bobbins, both between bobbins spun on adjacent spindles and between bobbins spun on the same spindle. The authors hope to obtain data on the extent of this variation and to suggest suitable modifications to the main solution to allow for this. It is not expected that such modifications will radically affect the solutions given in the present paper.

(iii) *Doffing patrols.* When a cheese or cone is full, one patrol is lost while the full package is being removed by hand (a "doffing" patrol). In practice, yarn from say 5 to 20 full supply bobbins is required to fill a cheese or cone. In the initial solution doffing patrols are ignored, but a modification at a later stage (Section 2.3) allows for them.

(iv) *Servicing time.* In practice the servicing time is of the order of 5–10 sec. and the patrolling time from 1–10 min. (seldom less than 2 min.). The servicing time does not always represent a loss of unwinding time: a spindle which is running when the knotting unit arrives continues to unwind yarn while the unit is present. In the initial solution, therefore, servicing time is ignored. A simple modification (Section 2.4) gives the result for the case in which the servicing time is assumed to be wasted in every patrol. The true value of the efficiency will lie between the values obtained without and with this modification.

2. Single Spindle Case

2.1 *Random Breaks Ignored*

Let the unwinding time of the bobbin be denoted by l, the patrolling time by T. When $T \geq l$, and there are no random breaks, a single patrol

[2] In practice μ is usually small, and if this is so it is approximately equal to the probability of an end down in a unit of yarn length.

suffices to unwind the bobbin; but when $T < l$, the number of patrols required depends on the relation between T and the factors or submultiples of l. In fact, if $T = l/i$, where i is a positive integer, exactly i patrols will be required to unwind the bobbin; and if $T > l/i$ but $< l/(i-1)$, the number of patrols required will still be i, for the first $i-1$ patrols occupy a time less than l, but the yarn remaining on the bobbin can be unwound within the next patrol. Thus when $l/(i-1) > T \geq l/i$, i patrols are required to unwind the bobbin. This is true when $T < l$, i.e., $i = 2, 3, 4, \ldots$; but we can include the case $T \geq l$ within the same statement by taking $i = 1$ to mean simply that $T \geq l$.

Now when i patrols are required, the total running time is iT and the unwinding time is of course l, so that the efficiency E is given by

$$E = l/iT \tag{2}$$

It is important to note that Equation 2 holds only when T lies in the range

$$l/(i-1) > T \geq l/i \tag{3}$$

where $i = 1, 2, 3, \ldots$; in particular, when $T = l/i$ (a submultiple of l), Equation 2 gives $E = 1$.

To find the relation between E and T for a given value of l, suppose that T initially has a value greater than l, and that it decreases. Initially the range, Equation 3, within which T lies is given by $i = 1$, but as it passes through the values l, $l/2$, $l/3$, . . . , it passes successively into ranges given by $i = 2, 3, 4, \ldots$ respectively, and the value of i used in Equation 2 must be increased by one unit at each passage through a submultiple of l. For values of T *between* $l/(i-1)$ and l/i the relation between E and T is given by Equation 2, but as T decreases *through* the value l/i there is a discontinuous change in E: when $T = l/i$, Equation 2 gives $E = 1$, but when T is a little less than l/i, it lies in the range $l/i > T \geq l/(i+1)$, so that from Equation 2 E will be calculated from the formula $l/(i+1)T$, and will therefore be a little greater than $i/(i+1)$.

The graph of E against T is thus as shown in Figure 1, the curves being arcs of hyperbolas, and E being unity at all the maxima.

2.2 *Random Breaks Taken into Account*

(i) $T \geq l (i = 1)$. In this case the effect of random breaks is easily seen. In the absence of breaks a single patrol suffices to unwind the bobbin, and each break necessitates an extra patrol. Since the average number of breaks is μl, the average number of patrols needed to unwind the bobbin is $\mu l + 1$, and the average efficiency is

$$\bar{E} = l/T(\mu l + 1) \tag{4}$$

This is the familiar solution applicable to existing winding machines where the automatic knotting unit cannot pass a running spindle.

(ii) $T < l$. As in paragraph 2.1, the relation between T and the submultiples of l is important. Assume therefore that

$$l/(i-1) > T \geq l/i \ (i = 2, 3, 4, \ldots)$$

so that i is the number of patrols required in the ab-

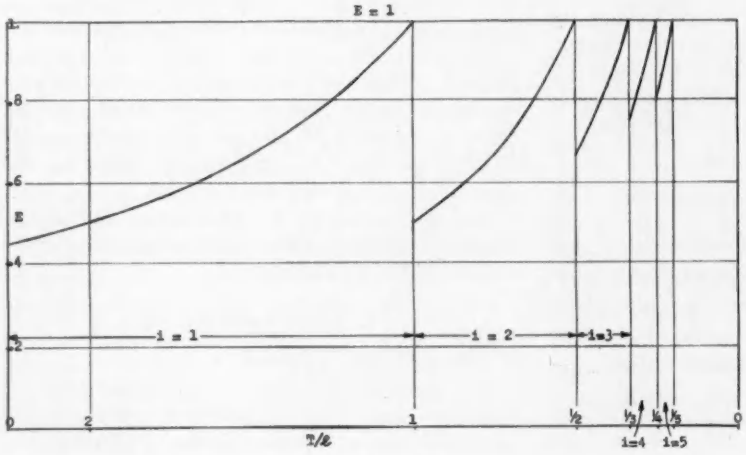

Fig. 1. Relationship between machine efficiency and patrolling time.

sence of breaks. The analysis is helped by the introduction of the notation $\bar{t}$ for the amount of yarn still to be unwound after $i-1$ patrols when there are no breaks (i.e., $\bar{t} = l - (i-1)T$), and t for the amount of yarn which would have to be added to the bobbin so that *exactly* i patrols would be needed to unwind it in the absence of breaks (i.e., $t = iT - l$). Since

$$l = (i-1)T + \bar{t} = iT - t \tag{5}$$

and since $(i-1)T < l$ and $iT \geq l$, it follows that

$$t + \bar{t} = T \tag{6}$$

where $0 < \bar{t} \leq T$ and $0 \leq t < T$. Figure 2(i) shows the relationship between the symbols l, T, i, t and $\bar{t}$.

To find the effect of breaks here is more difficult than in the case $T \geq l$. In the absence of breaks, i patrols are required. Assume first that there is only one break. If it occurs within the first $\bar{t}$ of the first patrol, the part left exceeds $(i-1)T$ but is less than iT, and therefore requires i patrols to be unwound; thus the break has necessitated an extra patrol. But if the break occurs within the last t of the first patrol, the part left lies between $(i-2)T$ and $(i-1)T$, and therefore requires $i-1$ patrols to be unwound; thus the break has caused no change in the total number of patrols required. This is illustrated in parts (ii) and (iii) of Figure 2. The same applies to a break in any patrol, and to the effect of more than one break. If there is only one break (in any patrol) it may or may not necessitate an extra patrol, according to its position within the patrol. If there are two breaks, each may or may not necessitate an extra patrol, so that the total number of *extra* patrols necessitated by the breaks may be 0, 1, or 2 (though there are exceptional cases when i (i.e., l) is small: e.g. when $i = 2$, i.e., l lies between T and $2T$, if the first break does not necessitate an extra patrol the second one does—it is impossible here for two breaks to have no effect on the total number of patrols required). In general, if there are r breaks, the number s of *extra* patrols they necessitate can take any value from 0 to r (if i is large enough), depending on the positions of the breaks on the supply bobbin. It is necessary therefore to determine P_s, the probability that in the given case s extra patrols will be required as a result of breaks, so as to get the average number of patrols required, $\bar{N}$, and hence the average efficiency $\bar{E}$. This is the problem considered by Howie and Shenton: their result is that

$$\bar{E} = l/\bar{N}T \tag{1}$$

where

$$\bar{N} = (1+\mu l)\left(\frac{1-e^{-i\mu T}}{1-e^{-\mu T}}\right) - \mu T e^{-\mu T}\,\frac{\{1-e^{-(i-1)\mu T} - (i-1)e^{-(i-1)\mu T}(1-e^{-\mu T})\}}{(1-e^{-\mu T})^2} \tag{7}$$

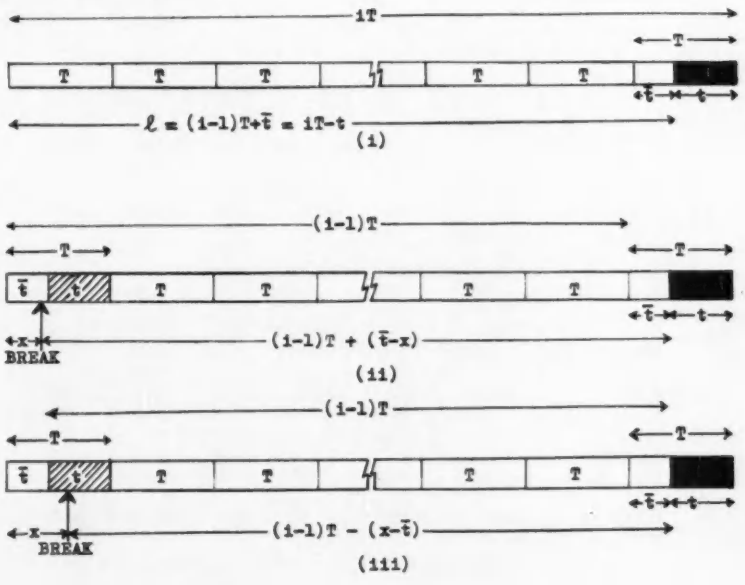

Fig. 2. (i) Relationship between the symbols l, T, i, t and $\bar{t}$. (ii) The effect of a break in the first $\bar{t}$ of the first patrol. (iii) The effect of a break in the last t of the first patrol.

If we put $i = 1$ in this result we arrive at Equation 4; if we put $\mu = 0$ the right-hand side of Equation 7 takes the indeterminate form 0/0, so we must consider what limit it approaches as μ tends to 0. By expansion of the exponentials it may be shown that this limit is i, so that the expression for the average efficiency $\bar{E}$ reduces to l/iT, in agreement with Equation 2 for the no-break case.

It is required to find how $\bar{E}$ varies with T for a given value of l. Firstly, it must be noted that $\bar{E}$ is given by Equations 1 and 7 only when T lies in the range

$$l/(i-1) > T \geq l/i \tag{3}$$

Secondly, the relation between $\bar{E}$ and T is made clearer if we introduce the notation $\bar{E}_1(i)$ and $\bar{E}_2(i)$ for the values of $\bar{E}$ obtained by substituting the extreme values $T = l/(i-1)$ and $T = l/i$ respectively in Equations 1 and 7. $\bar{E}_2(i)$ is simply the average efficiency when $T = l/i$, but $\bar{E}_1(i)$ is *not* the average efficiency when $T = l/(i-1)$, because the range (Equation 3) for which the result of Equations 1 and 7 is applicable does not include the value $T = l/(i-1)$. $\bar{E}_1(i)$ can be regarded as a quantity introduced for mathematical convenience or as the *limit* which the average efficiency approaches as T tends to $l/(i-1)$ through *smaller* values. The actual average efficiency when $T = l/(i-1)$ is got by observing that T now is included in the range

$$l/(i-2) > T \geq l/(i-1)$$

(i.e., Equation 3 with i replaced by $i-1$), so that we must now replace i in Equation 7 by $i-1$. In other words, to find the average efficiency when $T = l/(i-1)$, we change i in Equation 7 into $i-1$ and then substitute $T = l/(i-1)$ in Equations 1 and 7: this is the quantity which is represented by $\bar{E}_2(i-1)$ in the present notation. By actual substitution in Equations 1 and 7 we can show in a few lines of algebra that

$$\frac{1}{\bar{E}_1(i)} - \frac{1}{\bar{E}_2(i-1)} = \frac{e^{-\mu l}}{i-1} \tag{8}$$

and the right-hand side here is essentially positive: thus

$$\bar{E}_2(i-1) > \bar{E}_1(i)$$

i.e., the average efficiency when $T = l/(i-1)$ exceeds the limit which the average efficiency approaches when T tends to $l/(i-1)$ through smaller values.

Now suppose that T takes a value between $l/(i-2)$ and $l/(i-1)$, and decreases. The average efficiency increases until it attains the value $\bar{E}_2(i-1)$ when $T = l/(i-1)$. As T continues to decrease, $\bar{E}$ decreases discontinuously at $T = l/(i-1)$ and thereafter increases from the value $\bar{E}_1(i)$. It continues to increase until it attains the value $\bar{E}_2(i)$ when $T = l/i$, where it decreases discontinuously and then increases from $\bar{E}_1(i+1)$, and so on.

It follows that the expression given by Equations 1 and 7 for $\bar{E}$ has properties similar to those of

TABLE I. Values of $\bar{E}_1(i)$ and $\bar{E}_2(i)$

μl		i = 1	2	3	4	5	6	7	8	9	10	11
1.0	$\bar{E}_1(i)$	0	.4223	.6102	.7064	.7647	.8036	.8316	.8525	.8689	.8819	.8926
	$\bar{E}_2(i)$	.5	.6873	.7734	.8225	.8542	.8762	.8925	.9050	.9149	.9229	.9296
0.8	$\bar{E}_1(i)$	0	.4446	.6274	.7220	.7757	.8130	.8397	.8597	.8752	.8877	.8979
	$\bar{E}_2(i)$	.5555	.7303	.8096	.8498	.8771	.8960	.9099	.9205	.9288	.9356	.9412
0.6	$\bar{E}_1(i)$	0	.4654	.6427	.7318	.7854	.8211	.8466	.8658	.8807	.8926	.9024
	$\bar{E}_2(i)$	.625	.7803	.8449	.8802	.9024	.9177	.9288	.9373	.9440	.9494	.9538
0.4	$\bar{E}_1(i)$	0	.4830	.6551	.7413	.7930	.8275	.8521	.8706	.8850	.8965	.9059
	$\bar{E}_2(i)$	.7143	.8395	.8885	.9146	.9308	.9418	.9498	.9559	.9606	.9645	.9676
0.2	$\bar{E}_1(i)$	0	.4954	.6636	.7477	.7981	.8318	.8558	.8738	.8879	.8991	.9082
	$\bar{E}_2(i)$	.8333	.9110	.9393	.9540	.9629	.9689	.9733	.9766	.9791	.9812	.9829
0	$\bar{E}_1(i)$	0	.5	.6667	.75	.8	.8333	.8571	.875	.8889	.9	.9091
	$\bar{E}_2(i)$	1	1	1	1	1	1	1	1	1	1	1

When $\mu l = 0$, $\bar{E}_1(i) = (i-1)/i$. When $i = 1$, $\bar{E}_2(1) = 1/(1+\mu l)$.

Equation 2, as indicated by the graph of Figure 1, except that the value of $\bar{E}$ is no longer unity at all the maxima. Table 1 gives values of $\bar{E}_1(i)$ and $\bar{E}_2(i)$ for a range of values of μl and of i which should cover all cases likely to occur in practice. The graphs of Figure 3 show the variation of $\bar{E}$ with T for a similar range of values: they are accurate enough to be used for evaluation of efficiencies in actual cases.

2.3 *Allowance for Doffing Patrols*

For every N' bobbins completely unwound on a spindle, let an additional (doffing) patrol be required for manual removal of the full package. On the average, $\bar{N}$ patrols are required to unwind each bobbin, so that $\bar{N}N' + 1$ patrols are required, allowing for doffing, to unwind N' bobbins. Thus $\bar{E}_D$, the average efficiency allowing for doffing, is

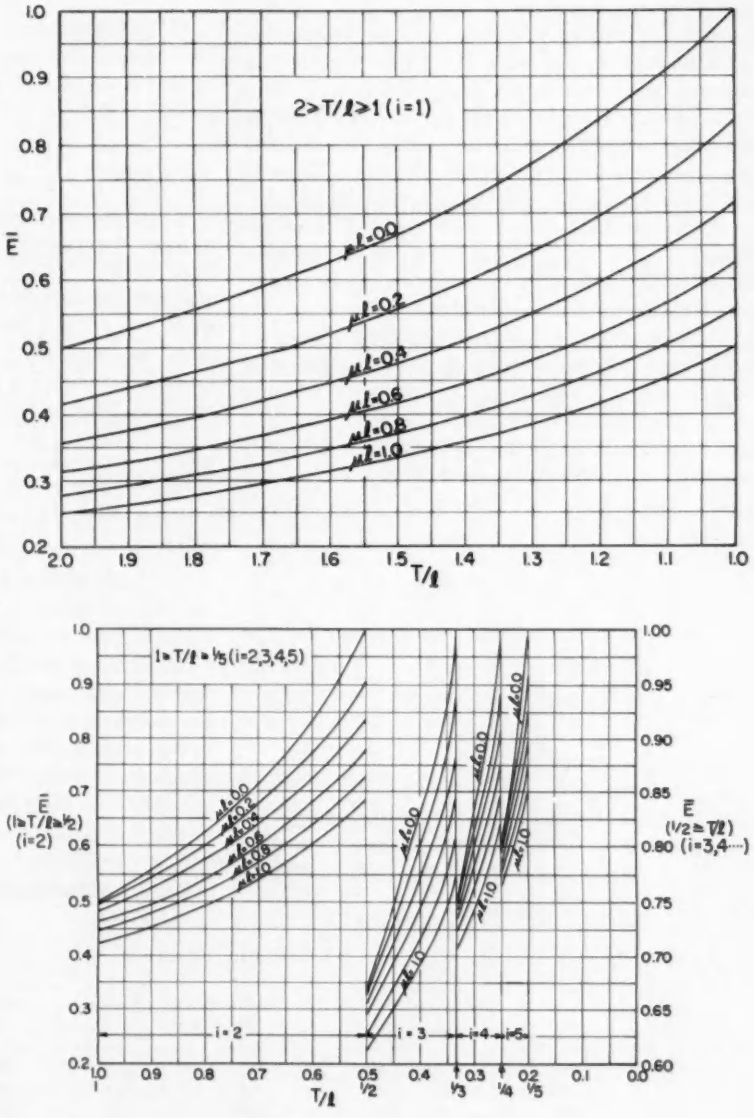

Fig. 3. General relationships between $\bar{E}$ and T/l for different breakage rates.

given by

$$\bar{E}_D = N'l/(\bar{N}N' + 1)T = \bar{E}\cdot N'/(N' + \bar{E}(T/l)) = \bar{E}\delta \quad (9)$$

say, where $\delta = N'/(N' + \bar{E}(T/l))$ is a "doffing factor." Table II gives values of δ for a suitable range of μl and of i, and for $N' = 5$ and $N' = 20$.

2.4 *Allowance for Servicing Time*

Assume that in every patrol the knotting unit spends at the spindle a servicing time S which is wasted, i.e., during this time no unwinding takes place and no breaks can occur. Let T be the remaining part of the patrol, during which unwinding takes place provided that the yarn is not broken or the supply bobbin exhausted. Then the *number* of patrols required to unwind a bobbin of length l will depend, exactly as before, on the relation of T to l, but the actual time of each patrol is increased from T to $T + S$. It follows that every expression for efficiency above can be made to apply to this case if the factor T in the denominator is changed to $T + S$: i.e., $\bar{E}_S$, the average efficiency allowing for servicing time wasted in every patrol, is given by

$$\bar{E}_S = \bar{E}T/(T + S) = \bar{E}\sigma \quad (10)$$

TABLE II. Values of δ

	i					
μl	1	2	3	4	5	6
			$N' = 5$			
1.0	.91	.93	.95	.96	.97	.97
0.8	.90	.93	.95	.96	.96	.97
0.6	.89	.92	.94	.96	.96	.97
0.4	.88	.92	.94	.95	.96	.97
0.2	.86	.91	.94	.95	.96	.97
0	.83	.91	.94	.95	.96	.97
			$N' = 20$			
1.0	.98	.98	.99	.99	.99	.99
0.8	.97	.98	.99	.99	.99	.99
0.6	.97	.98	.99	.99	.99	.99
0.4	.97	.98	.98	.99	.99	.99
0.2	.96	.98	.98	.99	.99	.99
0	.95	.98	.98	.99	.99	.99

say, where $\sigma = T/(T + S)$ is a "servicing time factor."

In practice S remains more or less constant (at about 7 sec.) even when T is varied, so that σ depends only on T (strictly on the ratio $S{:}T$); in this respect it differs from the doffing factor δ. The values of σ for a suitable range of values of T and S are given in Table III.

2.5 *Applicability of These Results*

It is obvious that these results apply also to the case where the number of spindles exceeds one, provided that the supply bobbins on all the spindles have the same unwinding times.

2.6 *Example 1*

When the unwinding time l is 5 (min.) and the average number of yarn breaks per supply bobbin is (i) 1, (ii) $\frac{1}{2}$, (iii) 0, how does $\bar{E}$ vary with T? If the smallest possible value of T is (i) *3*, (ii) *2* (min.), what value will give maximum spindle efficiency? How are these results affected by allowance, as in Sections 2.3 and 2.4, for doffing ($N' = 5$) and for a servicing time of 7 sec.?

The Table for Example 1 gives values of machine efficiency for various values of T, calculated from the tables and graphs given.

From the table the following answers are obtained to the questions asked above:

When the doffing and servicing times are ignored and the minimum T is 3, the maximum value of $\bar{E}$ is 0.604, attained when $T = 3$, when $\mu l = 1$.

When the doffing and servicing times are ignored and the minimum T is 3, the maximum value of $\bar{E}$ is 0.704, attained when $T = 3$, when $\mu l = 0.5$.

When the doffing and servicing times are ignored and the minimum T is 3, the maximum value of $\bar{E}$ is 1.000, attained when $T = 5$, when $\mu l = 0$.

When the doffing and servicing times are ignored and the minimum T is 2, the maximum value of $\bar{E}$ is 0.692, attained when $T = 2$, when $\mu l = 1$.

TABLE III. Values of σ

	T, min.													
S, sec.	10	9	8	7	6	5	4.5	4	3.5	3	2.5	2	1.5	1
10	.98	.98	.98	.98	.97	.97	.96	.96	.95	.95	.94	.92	.90	.86
7	.99	.99	.99	.98	.98	.98	.97	.97	.97	.96	.96	.94	.93	.90
5	.99	.99	.99	.99	.99	.98	.98	.98	.98	.97	.97	.96	.95	.92

Table for Example 1. Values of $\bar{E}$

	μl	T, min. 10	5	3	2.5	2	1.6	1.25
(a) Doffing and servicing time ignored	1	.25	.50 , .422	.604	.687, .610	.692	.773, .706	.823, .765
	0.5	.339	.670, .474	.704	.810, .649	.761	.867, .737	.897, .789
	0	.50	1.00 , .50	.833	1.00 , .667	.833	1.00 , .750	1.00 , .80
(b) Doffing ($N' = 5$) allowed for	1	.227	.455, .389	.563	.643, .575	.656	.735, .674	.790, .737
	0.5	.299	.591, .433	.651	.749, .609	.715	.820, .703	.859, .759
	0	.416	.833, .455	.757	.909, .625	.781	.938, .714	.952, .769
(c) Servicing time (7 sec.) allowed for	1	.247	.489, .412	.581	.656, .583	.654	.722, .660	.753, .700
	0.5	.335	.655, .463	.678	.774, .620	.719	.810, .689	.820, .722
	0	.494	.977, .489	.802	.955, .637	.787	.935, .701	.915, .732
(d) Doffing and servicing time allowed for	1	.224	.445, .380	.542	.614, .549	.620	.687, .630	.723, .674
	0.5	.296	.578, .423	.627	.716, .582	.676	.766, .657	.786, .694
	0	.411	.814, .445	.729	.868, .597	.738	.877, .667	.871, .703

The values of T which are of interest are l and its submultiples, i.e., 5, 2.5, 1.6, . . . , and the extreme values mentioned in the example, namely 3 and 2. For completeness a value greater than l, namely 10, is given in the table.

For the reasons given above, two values of $\bar{E}$ are of interest when $T = l$ or a submultiple, namely the upper and lower values of the discontinuous jump in $\bar{E}$ at such a value of T. In the table, at each submultiple the first (higher) value of $\bar{E}$ is the actual average efficiency at that value of T, the second (lower) value is the one from which $\bar{E}$ increases as T decreases further.

When the doffing and servicing times are ignored and the minimum T is 2, the maximum value of $\bar{E}$ is 0.810, attained when $T = 2.5$, when $\mu l = 0.5$.

When the doffing and servicing times are ignored and the minimum T is 2, the maximum value of $\bar{E}$ is 1.000, attained when $T = 5$ or 2.5, when $\mu l = 0$.

These conclusions are not much affected by allowing for doffing and for servicing time.

Notes. (i) The graph of $\bar{E}$ against T for each given value of μl is the same as the corresponding graph of Figure 3. (ii) The values of $\bar{E}$ in (a) are obtained from the graphs of Figure 3, using linear interpolation in the case $\mu l = 0.5$. (iii) The figures in (b) are those in (a) multiplied by the appropriate factor from Table II. The figures in (c) are those in (a) multiplied by the appropriate factor from Table III. The figures in (d) are those in (a) multiplied by the appropriate factors from Tables II and III.

From the graph of Figure 3 can be seen the advantage to be gained from lower values of T when the breakage rate is high.

3. Multiple Spindle Case

Let there be N spindles and assume that the supply bobbins are not all the same length. For definiteness, suppose that there are three distinct bobbin lengths l, m, n being unwound on N_l, N_m, N_n spindles respectively ($N = N_l + N_m + N_n$). Let $\bar{E}_l$, $\bar{E}_m$, $\bar{E}_n$ be the average efficiencies for spindles with bobbins of lengths l, m, n respectively. If the machine is run for τ seconds, on the average $\tau\bar{E}_l$, $\tau\bar{E}_m$, $\tau\bar{E}_n$ are the numbers of seconds spent in actual unwinding on the respective spindles. Thus of the $N\tau$ spindle-seconds $\tau(N_l\bar{E}_l + N_m\bar{E}_m + N_n\bar{E}_n)$ are, on the average, spent in actual unwinding, so that the overall average efficiency $\bar{E}$ is given by

$$\bar{E} = (N_l\bar{E}_l + N_m\bar{E}_m + N_n\bar{E}_n)/N \qquad (11)$$

This argument applies whether random breaks are taken into account or ignored (when they are ignored we have actual efficiencies E, E_l, etc. instead of average efficiencies $\bar{E}$, $\bar{E}_l$, etc.)

3.1 *Random Breaks Ignored*

3.11 *Expressions for overall efficiency.* It is convenient to write l_i for l/i, m_j for m/j, n_k for n/k where i, j, k are positive integers. Let

$$l_{i-1} > T \geq l_i, \quad m_{j-1} > T \geq m_j, \quad n_{k-1} > T \geq n_k,$$

where $i, j, k = 1, 2, 3, \ldots$ (the case $i = 1$ is simply that in which $T \geq l$). Then from Equation 2

$$E_l = l_i/T, \quad E_m = m_j/T, \quad E_n = n_k/T,$$

so that Equation 11 gives for the overall efficiency

$$E = (N_l l_i + N_m m_j + N_n n_k)/NT \qquad (12)$$

For each spindle (as seen in Section 2.1) the efficiency increases as T diminishes except for the discontinuous drop in efficiency as T decreases through a value which is a factor of the appropriate unwinding time. Thus E as given by Equation 12 has the same general properties as Equation 2, the values of T at which drops in E occur being the submultiples of all the unwinding times, and the maxima being in general not unity, though unity is of course not impossible. The graph of Example 3 illustrates this (Section 3.4).

The submultiples of the unwinding times are thus critical values of T, and in determining T for maximum efficiency it will be useful to know the efficiency for T at, and just below, a submultiple. Suppose that

$$m_{j-1} > l_{i-1} \geq m_j \quad \text{and} \quad n_{k-1} > l_{i-1} \geq n_k$$

then when $T = l_{i-1}$ the overall efficiency E is (from Equation 12)

$$E = (N_l l_{i-1} + N_m m_j + N_n n_k)/N l_{i-1} \qquad (13)$$

and when T is just below l_{i-1}, E is just above the value given by

$$E = (N_l l_i + N_m m_j + N_n n_k)/N l_{i-1} \qquad (14)$$

3.12 *Procedure for determining T for maximum efficiency.* It is possible to calculate efficiencies exactly from Equations 12, 13, and 14 by a simple arithmetical technique, and hence to find whether maximum efficiency is attained by setting T at the minimum value available on the machine or at some higher submultiple of an unwinding time.

The procedure is most easily described for the particular case in which there are only three spindles, with different unwinding times on all three: i.e., $N_l = N_m = N_n = 1$. Then Equations 12, 13, 14 become

$$E = (l_i + m_j + n_k)/3T \qquad (12a)$$

$$E = (l_{i-1} + m_j + n_k)/3l_{i-1} \qquad (13a)$$

and

$$E = (l_i + m_j + n_k)/3l_{i-1} \qquad (14a)$$

respectively.

First, the values $l_1, l_2, l_3, \ldots$ are written in a line, suitably spaced; then in the next line $m_1, m_2, m_3, \ldots$ are written, in the correct spaces relative to the values of the l's (if a value m_j equals a value l_i, it is written below it); and in the next line $n_1, n_2, n_3, \ldots$ are written, in the correct spaces relative to the values of both l's and m's. Then for a value T of the patrolling time, $3E$ is given by the sum of the entries in the three lines of this table immediately to the right of (or vertically in line with) T, divided by T. In particular, for $T = l_i$, $3E$ is the sum of l_i and the entries in the other lines immediately to the right of, or vertically below, l_i, divided by l_i; and for T just below l_i, $3E$ is just above the sum of the entries in all the lines immediately to the right of l_i, divided by l_i. The process is illustrated in Example 3 (Section 3.4).

Suppose now that there are N spindles, N_l, N_m, N_n of them having bobbins of length l, m, n respectively ($N = N_l + N_m + N_n$). Then from Formulae 12, 13, and 14 it is clear that the above process can be used with only slight modification. After the values $l_1, l_2, l_3, \ldots, m_1, m_2, m_3, \ldots, n_1, n_2, n_3, \ldots$ have been set out in the correct relative positions the l's are multiplied by N_l, the m's by N_m, and the n's by N_n, *but their positions in the table are not altered.* To calculate NE we sum these products in exactly the same way as values of l's, m's and n's were summed in the simpler case, and divide by the same quantity as before. This process is illustrated in Example 4 (Section 3.4).

If it is preferred, the process of Section 3.2 (reading efficiencies for individual spindles from the graph or table instead of actually calculating them) can be used even when random breaks are being ignored.

3.2 *Random Breaks Taken into Account*

The Formula 11 still applies, but since average efficiencies of individual spindles are now given by formulae of the type of Equations 1 and 7 instead of 2, it is no longer possible to express the overall efficiency in the simple form of Equation 12. It is still true that submultiples of the unwinding times are critical values of T, and that as T decreases through any one of them the overall efficiency drops discontinuously and rises steadily until the next submultiple is reached. The tabular arrangement described in Section 3.12 will still be useful, but it is no longer possible to calculate from a simple ratio the efficiency when T has any specified value; instead, the average efficiencies for the individual spindles can be read from the graphs of Figure 3 or, when T is a submultiple of an unwinding time (which is obviously a specially informative value), from Table I, and then combined according to Formula 11. This process is illustrated in Example 5 (Section 3.4).

3.3 *Allowances for Doffing Patrols and Servicing Time*

The effects of doffing patrols and of servicing time S (wasted in every patrol) can be allowed for in the multiple spindle case. The doffing factor δ of Section 2.3 varies with l and with the efficiency for the individual spindles: δ must therefore be applied to the efficiencies $\bar{E}_l$, $\bar{E}_m$, $\bar{E}_n$ of Equation 11 separately before they are substituted in that formula. (This means that when random breaks are being ignored it is simpler to use the process of Section 3.2 than that of Section 3.12—see the last paragraph of Section 3.12.) The servicing time factor σ of Section 2.4, on the other hand, does not change from one spindle to another, so for given T and S this factor may be immediately applied to the overall efficiency $\bar{E}$ of Equation 11.

3.4 *Examples 2 through 6*

Example 2. Considering the two spindles supplied with bobbins having unwinding times respectively $l = 10$, $m = 5$, the overall efficiency $\bar{E}$ is given in Table for Example 2 for widely differing breakage rates (though the same rate on both spindles) for the very simple cases when $T = 10$ and $T = 5$.

Thus the advantage of putting $T < l$ is greatest when there are widely different unwinding times (as here) and when the breakage rate is high (as in Examples 1 and 5). In the present example the gain in efficiency in reducing T from 10 to 5 is practically independent of the breakage rate.

It is perhaps worth noting that in practice breakage rates of $\mu l < 0.1$ are not uncommon.

Example 3. Considering four spindles supplied with bobbins having unwinding times respectively 10, 9, 7, 6, find the value of T for maximum efficiency when the minimum possible value of T is (i) 3, (ii) 4, breaks being ignored.

Here E is the efficiency at the appropriate submultiple of l, etc.; E' is the value to which the efficiency drops as T decreases through this value. The graph of E against T is shown in Figure 4.

(i) If the minimum possible value of T is 3, the maximum efficiency is $3.67/4 = 0.92$, and is attained when $T = 3.5$.

(ii) If the minimum possible value of T is 4, the efficiency when $T = 4$ is $(3.33 + 3 + 3.5 + 3)/4 \times 4 = .80$; therefore the maximum efficiency is 0.805, attained when $T = 7$.

Example 4. Considering the same problem as for Example 3 but now there are 10 spindles, of

Table for Example 2

Average breaks per bobbin	T	$\bar{E}$
$\mu l = \mu m = 0$	10	$\frac{1}{2}(1.00 + .50) = .75$
	5	$\frac{1}{2}(1.00 + 1.00) = 1.00$
$\mu l = .4$, $\mu m = .2$	10	$\frac{1}{2}(.72 + .42) = .57$
	5	$\frac{1}{2}(.83 + .83) = .83$
$\mu l = 1$, $\mu m = .5$	10	$\frac{1}{2}(.50 + .34) = .42$
	5	$\frac{1}{2}(.69 + .67) = .68$

Table for Example 3

l	10				5		3.33	2.50	
m		9				4.5		3	
n			7				3.5		2.33
p				6				3	
$4\bar{E}$	3.20	3.00	3.22	3.17	3.20	3.19	3.67	3.50	3.61
$4\bar{E}'$	2.70	2.50	2.72	2.67	2.87	2.86	3.33	3.26	

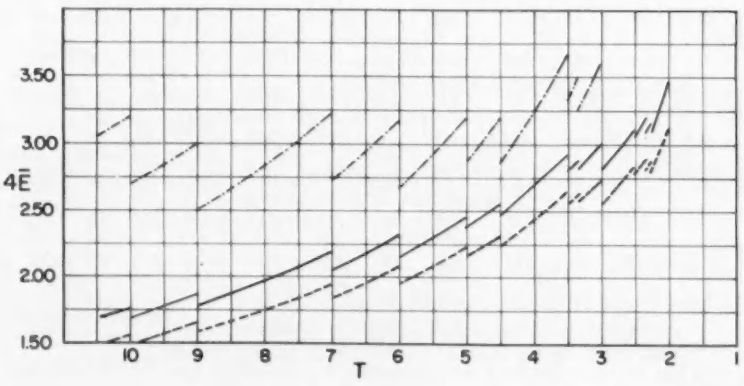

Fig. 4. Graph for Example 3 ——·——·——. Graph for Example 5, ignoring doffing and servicing ——; allowing for doffing ($N' = 5$) and servicing (7 sec.) – – – – – –.

Table for Example 4

l	40(10)				20(5)			$13.\dot{3}(3.\dot{3})$		10(2.5)	
m		27(9)				13.5(4.5)			9(3)		
n			14(7)				7(3.5)				$4.\dot{6}(2.\dot{3})$
p				6(6)					3(3)		
$10E$	8.70	7.44	7.65	7.75	8.70	8.19	9.24	9.01	8.89		
$10E'$	6.70	5.95	6.64	7.25	7.37	7.19	8.57	8.01			

Here the bracketed figures are the values l_i, i.e., the values of T at which the efficiencies apply; the unbracketed figures represent l_i multiplied by the appropriate values of N_l, i.e., the values used in calculating the overall efficiency.

which 4 have time 10, 3 have time 9, 2 have time 7, and 1 has time 6.

(i) If the minimum possible value of T is 3, the maximum efficiency is 0.924, and is attained when $T = 3.5$.

(ii) If the minimum possible value of T is 4, the efficiency when $T = 4$ is $(13.33 + 9 + 7 + 3)/40 = 0.808$; therefore the maximum efficiency is 0.870, and is attained when $T = 10$ or 5.

Example 5. Considering the same unwinding times as for Example 3 but allowing for yarn breaks, with $\mu = 0.1$ for all the bobbins, i.e., $\mu l = 1$, $\mu m = 0.9$, $\mu n = 0.7$, $\mu p = 0.6$, the values for efficiency under various conditions are given in the Table for Example 5.

Notes referring to the Table for Example 5. (i) The bold face figures in Column 2 are submultiples of the l's, etc. At these values the efficiency drops discontinuously. (ii) The individual efficiencies in Column 3 are read from the graphs of Figure 3. (iii) The figures in Column 5 are the sums of the efficiencies in Column 3. The figures in Column 6

Table for Example 5

(1)	(2) Ratio "T/l"				(3) Individual spindle efficiency				(4) $\delta(N' = 5)$				(5)* 4 × overall efficiency ($4\bar{E}$)	(6)†	(7)	(8)‡
T	l	m	n	p	l	m	n	p	l	m	n	p			σ	$4\bar{E}$
10	**1**	.11	1.43	1.67	.500	.475	.413	.371	.91	.90	.89	.89	1.759	1.580	.99	1.564
					.423				.93				1.682	1.510		1.495
9	.9	**1**	1.29	1.5	.455	.528	.457	.417	.93	.90	.89	.89	1.857	1.676	.99	1.659
						.436				.93			1.765	1.606		1.590
7	.7	.78	**1**	1.17	.540	.515	.591	.530	.93	.93	.89	.89	2.176	1.979	.98	1.939
							.455				.92		2.040	1.871		1.834
6	.6	.67	.86	**1**	.603	.574	.506	.625	.93	.93	.92	.89	2.308	2.116	.98	2.074
								.465				.92	2.148	1.988		1.948
5	**1/2**	.56	.71	.83	.687	.652	.581	.529	.93	.93	.92	.92	2.449	2.266	.98	2.221
					.610				.95				2.372	2.162		2.163
4.5	.45	**1/2**	.64	.75	.645	.709	.626	.571	.95	.93	.92	.92	2.551	2.373	.97	2.302
						.619				.95			2.461	2.302		2.233
3.5	.35	.39	**1/2**	.58	.750	.714	.755	.697	.95	.95	.92	.92	2.916	2.727	.97	2.645
							.635				.94		2.796	2.629		2.550
$3.\dot{3}$	**1/3**	.37	.475	.56	.773	.739	.655	.717	.95	.95	.94	.92	2.884	2.712	.97	2.631
					.706				.96				2.817	2.655		2.575
3	.3	**1/3**	.43	**1/2**	.745	.791	.695	.780	.96	.95	.94	.92	3.011	2.838	.96	2.724
						.714		.643		.96		.94	2.797	2.658		2.552
2.5	**1/4**	.28	.36	.42	.823	.786	.783	.717	.96	.96	.94	.94	3.109	2.955	.96	2.837
					.765				.97				3.051	2.907		2.791
$2.\dot{3}$	.23	.26	**1/3**	.39	.788	.819	.827	.754	.97	.96	.94	.94	3.188	3.037	.95	2.885
							.728				.96		3.089	2.958		2.810
$2\frac{1}{4}$	.225	**1/4**	.32	.38	.805	.837	.745	.765	.97	.96	.96	.94	3.152	3.019	.95	2.868
						.771				.97			3.086	2.963		2.815
2	**1/5**	.22	.29	**1/3**	.854	.866	.890	.845	.97	.97	.96	.94	3.455	3.317	.94	3.118
N_l	—	—	—	—	4	3	2	1	—	—	—	—	—	—	—	—

* In obtaining the figures in Column 5, δ was ignored.
† In obtaining the figures in Column 6, δ was taken into account.
‡ The figures in Column 8 are four times the overall efficiency, allowing for both δ and σ.

are the sums of the products of the corresponding figures in Columns 3 and 4. (iv) The graphs of the figures in Columns 5 and 8 against T are shown in Figure 4.

Example 6. The same problem as for Example 5, but now there are ten spindles, of which four have unwinding time 10, three have time 9, two have time 7, and one has time 6.

The method is the same as that of Example 5, except that the efficiencies in Columns 3 of the Table for Example 5 are multiplied by N_t, etc. (the values at the bottom of Columns 3), and the products are added to give $10\bar{E}$ for the figures of Column 5.

Literature Cited

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Some Observations on the Relationship between Mechanical Properties and Submicroscopic Structure of Cellulosic Tire Cords[1]

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Introduction

One of the important factors in the changing pattern of our economy in the last decade has been the development of improved road systems and automobiles capable of maintaining very high speeds for prolonged periods of time. Speed and comfort requirements, together with a demand for smaller diameter tires and lower operating pressure, have put a vastly increased strain on tires and, in particular, on the reinforcing body fabric. New requirements for stronger tire fabrics to withstand heavier loads, more severe flexing, and higher operating temperatures, as well as vigorous competition in the rapidly growing market, have initiated a considerable amount of research work to develop new, or improved fibers for tire body reinforcement.

Most of the high tenacity yarns used today in tires and for other industrial end uses are of cellulosic origin. An attempt will be made to describe the physical properties as well as the fine structure of such yarns, particularly those made by the viscose process.

[1] A similar paper was presented to the First Cellulose Conference held at the Cellulose Research Institute, Syracuse, New York, in 1958. The original paper was modified to include some new material, and presented at the 137th meeting of the American Chemical Society, Cleveland, 1960.

The presence of highly ordered regions in cellulose fibers, as revealed by X-ray diffraction, led to the speculation that the quantity and disposition of these regions may be reflected in the gross mechanical properties of the fibers [9]. Initially these ordered regions were pictured as crystallites embedded in an amorphous matrix. Later investigators [1, 2] coping with the relative incompatibility of accessibility and crystallinity measurements, have referred to "various degrees of lateral order," and recently Howsmon [11] has introduced the concept of crystallinity as a statistical distribution in the density of hydrogen bonds from one volume element to another in the fibers. By comparing accessibility and crystallinity data obtained in different ways, it is possible to make deductions concerning the distribution of order in cellulose fibers. The relevance of some of these parameters in connection with the mechanical properties of the fiber, as well as the limitations imposed by the lack of more precise methods of investigation, will be discussed.

Physical Properties

The two most important improvements in physical properties are increased tensile strength and increased fatigue resistance. Spectacular gains in these properties have been achieved recently (Table I).

TABLE I. Progress in Cellulosic Tire Cord Properties

Product	Strength, lb*	Fatigue rating†	Year
Tenasco‡ Regular	30	—	1953
Tenasco 201	34	100	1955
Tenasco 301	37	82	1956
Tenasco 401	38.5	135	1957
Tenasco 401-a	38.5	128	1958
Tenasco 501	40.5	140	1959
Super A**	33	62	1955
Super Super A	35	57	1956

* 2 × 1650 denier, 11.3 × 10.6 twist.
† Based on Firestone Compression Fatigue Test.
‡ Tenasco is a Courtaulds Limited trade mark for high tenacity yarns.
** A related series of commercially available competitive yarns.

The marked advance in performance exhibited by these new high strength cellulose yarns has come about mainly because a large increase in strength has not been accompanied by any decrease in extensibility as is the case with Durafil and saponified acetate types of rayon. Cellulose fibers of the saponified acetate type have been produced with tenacities as high as 9–10 g./den., but these fibers have never found acceptance in the tire yarn field because of low extensibility and poor fatigue. As a matter of fact, it was believed until a few years ago that any increase in tenacity had almost necessarily to take place at the expense of extensibility and fatigue. The fact that the relatively high tenacities of the new viscose rayons have not been accompanied by a decrease in extensibility suggests that in the not too distant future an acceptable tire yarn with a tenacity of 8 or 9 g./den., which would correspond to a 50-lb. cord strength level, will be produced.

Fine Structure

Recent improvements in tensile and fatigue properties of high tenacity cellulosic yarns have been described. The purpose of this paper is to discuss our attempts to relate those improvements to fine-structure parameters such as crystalline content, crystallite size, orientation, etc.

Experimental

Chain Length

The present concept of cellulose fine structure is one of cellulose chains threading through regions of high and low order. It seems not unlikely that the average chain length as well as chain-length distribution should exert some influence on the mechanical properties of the fiber. Consequently, viscometric measurements of DP, as well as estimates of the low DP fractions by cupriethylene diamine extraction were carried out.

Visometric DP. The relative viscosity of an 0.25% solution of cellulose in 0.5 *M* cupriethylene diamine at 25° C. was determined by preswelling the sample in 0.167 *M* cupriethylene diamine and adding sufficient 1.0 *M* cupriethylene diamine solution to attain the required final concentration. Intrinsic viscosities were estimated by means of the equation [13]:

$$[\eta] = \frac{3.3}{0.25}\left[\eta^{1/3.3} - 1\right]$$

Finally, the DP was calculated using the relationship proposed by Mark [12]:

$$[\eta] = 1.33 \times 10^{-4} \times M^{0.905}$$

Low DP fraction. The average DP of the 10% fraction most soluble in cupriethylene diamine was rather arbitrarily chosen as an index of the low DP content. Samples were preswollen in 0.2 *M* cupriethylene diamine for ½ hr. and then an appropriate amount of 0.05 *M* cupriethylene diamine was added to give a final concentration of 0.145 *M*. The mixture of yarn and cupriethylene diamine after standing for 1 hr. under nitrogen was separated by centrifuging. The relative viscosity was measured on one portion of the supernatant solvent and cellulose on another portion. Intrinsic viscosity and DP were estimated as outlined previously.

By varying the relative quantities of solvent and cellulose, different proportions of cellulose are dissolved. The 10% value was obtained by interpolation from curves relating percent dissolved to average DP of the fraction dissolved. From these curves the quantity of material whose average DP was below 250 or 300 could also be obtained (Table II).

As a cross-check on the concordance of the DP measurements, the average DP when the entire sample was dissolved in 0.145 *M* cupriethylene diamine was compared with the results previously obtained for the average DP in 0.5 *M* cupriethylene diamine. In all cases excellent agreement was obtained.

This measurement can quite correctly be criticized on the basis that equilibrium is probably never established, and that the measurement is dominated by kinetic effects. There is no doubt that this pro-

cedure is not as good as a full fractionation of nitrates. However, we hoped that the results obtained would enable us to see if any extensive work in this area was justified.

Crystallinity

The two classic methods of determining the crystalline content of cellulose are X-ray diffraction and density measurements. The X-ray diffraction method [7] is sometimes criticized on the grounds that it is unable to resolve crystallites below a certain size. There are, in addition, difficulties in estimating background scattering. Density measurements, on the other hand, are subject to serious limitations in that inhomogeneities in the sample can cause large errors in estimating the density. It is well established that high tenacity yarns frequently contain microscopically visible inhomogeneities believed to be vacuoles filled with air. For fibers such as these, it is necessary to make an indirect estimation of density from refractive index measurements [18]. Recently attempts have been made to apply infrared adsorption measurements to the determination of crystallinity and orientation in cellulose [15]. It is hoped that this technique, which shows great promise, will be further developed and applied.

Crystallinity by X-ray diffraction. A ratio proportional to the quantity of crystalline material present was determined using the method developed by Hermans and Weidinger [20]. The principles involved have been described in several papers. The method consists in measuring the amorphous and crystalline contribution of the total scattered intensities and determining the degree of crystallinity as the ratio:

$$D\ (\text{cryst}) = \frac{I\ (\text{cryst})}{I\ (\text{cryst}) + I\ (\text{amorphous})}$$

The success of the method depends, among other things, on the elimination of all preferred orientation from the specimen. Elaborate techniques for "randomization" have been described by Hermans and Weidinger [20], and these were closely followed in the present work.

Perfection of crystalline lattice. A parameter believed to be a measure of crystallite lateral order or micelle perfection was obtained by determining the ratio of the following intensities [6]:

$$L = \frac{I\ (101) - I\ (\text{min.})}{I\ (101)}$$

where $I(101)$ refers to the intensity of the (101) reflection and $I(\text{min.})$ the minimum intensity in the region between the (101) and (10$\bar{1}$) reflections.

Geiger counter techniques for measuring diffraction intensities offer many advantages for studies of this type when quantitative results are sought. In this work a Norelco High Angle Geiger Counter Diffractometer was used. The conventional filtering procedure was altered somewhat in order that the recorded radiation be effectively monochromatic. By making measurements alternately with balanced Ni and Co filters, and subtracting the intensity measured when the Co filter is present from that obtained when the Ni filter is present, the emitted radiation was limited to CuKa.

Stenner and Brown [4] have found that cellulose IV occurs in small quantities in many regenerated fibers during drying. The equatorial reflection of cellulose IV at 5.5–6.0 lies at a point where variation in its sharpness and intensity must affect $I(\text{min.})$ as well as increasing the difficulty of estimation of background intensity. Consequently, conditions of drying and the variation in the amount of cellulose IV would affect seriously both the X-ray crystallinity and the lateral-order measurements. In spite of these objections, it was hoped that both methods would rank fibers in the correct order and with sufficient accuracy to allow some conclusions regarding crystallite size and perfection of crystallite lattice to be drawn.

Crystallite Length

Crystallite length was estimated by determining the levelling off basic DP of the hydrocellulose residue after hydrolysis in 2.5 HCl, following the work of Battista and Coppick [3].

Amorphous Fraction

The most difficult aspect of the over-all problem of cellulose fine structure is the nature and disposition of the sub-crystalline material. Our approach to the problem was largely chemical, i.e., we looked to accessibility data.

One must concede at the outset that any reagent vigorous enough to overcome morphological restraints and to penetrate cracks and crevices in the yarn is likely to precipitate structural rearrangements which will obscure the original structure. However, at the time that this work was undertaken, no other approach was readily available; therefore, we had

to rely on the chemical approach, realizing its limitations.

Measurements based on formylation. Nickerson [16] has shown that of the chemical methods for determining accessibility, formylation is among the most satisfactory. He demonstrated that the crystalline phase is not attacked by this reagent.

Samples extracted with 50/50 alcohol/ether mixture were formylated under nitrogen using 90% formic acid at 4° and 35° C. for 4 hr. The degree of formylation relative to dextrin under the same conditions was taken as a measure of the accessibility.

Measurements based on soda swelling. Soda swelling methods have been criticized on the grounds that the treatments themselves are likely to cause irreversible changes in structure, which can make the derived lateral-order distribution different from that existing in the original fibers. To combat that objection, a method was developed [17] which depends on progressively increasing the swelling of a fiber using sodium hydroxide up to 10% (wt./wt.) concentration at 25° C. and measuring the change in length which occurs in the swollen stage without removing soda. It is believed that with this method there is less likelihood of obscuring the original lateral order. Differential curves obtained from relaxed-length measurements have revealed marked differences between fibers.

Measurements were made on 75-cm. lengths of yarn, washed free of finish, and freely suspended under a load of 1.5×10^{-4} g./den. When the natural length in water was established, yarn samples were immersed successively in sodium hydroxide solutions of increased swelling power at 25° C. The variation in length was measured with a cathetometer. From a summative curve, a lateral order plot was obtained by segmented differentiation.

Measurements based on moisture regain. As a first approximation, the sorption ratio, which is the ratio of the moisture regain of any sample of cellulose to that of cotton at the same relative humidity, is considered to be directly proportional to the relative lateral order of the given sample and cotton at that humidity [10, 19]. Quarter-gram skeins suspended on quartz spirals were dried by vacuum pumping until no further change was noted and then conditioned to equilibrium at 60% RH at 25° C.

Measurements based on water imbibition. Yarn samples were wetted down thoroughly in water containing 0.01% Tween 20 for 15 min., then centrifuged at 1000 g. for 5 min. to remove excess water. The weight of water retained by the yarn related to its bone dry weight × 100 is the water of imbibition.

Orientation

The influence of orientation on the physical properties of cellulose has been discussed by many investigators [8]. The extent to which the crystalline fraction is oriented can be determined by X-ray diffraction measurements. Birefringence measurements are valuable in that they give a picture of the over-all orientation of both crystalline and amorphous fractions. Both types of measurement were carried out in an attempt to account for the mechanical properties of high tenacity yarns.

Optical orientation (birefringence). The refractive indices parallel and perpendicular to the fiber axis were measured by the Becke line technique using

TABLE II. Degree of Polymerization of High Strength Cellulose Yarns

Yarn	Tenacity*	Whole sample	Av. DP of most easily dissolved 10%	% of yarn whose av. DP is below	
				250	300
Durafil	5.6	415	220	33	50
Sapon. acet.	7.1	290	200	90	100
Toramomen	3.5	520	—	—	—
Textile	2.1	280	185	32	100
Tenasco Reg.	3.6	380	—	—	—
Tenasco 201	4.2	380	290	1.5	20.0
Tenasco 301	4.5	380	275	2.0	20.0
Tenasco 401	5.2	420	350	0.0	0.0
Tenasco 401-a	4.5	365	260	8.0	50.0
Tenasco 501	5.2	365	260	8.0	50.0
Super A	4.4	275	255	4.0	100
Super Super A	4.7	325	275	7.5	13.0

* Conditioned filament tenacity in g./den.

TABLE III. Crystallinity Data

Yarn	Crystallinity		Cryst. perfection, intensity ratio	Levelling off DP a.g.u.†
	X-Ray	Density[20]		
Textile	50	45	42	20
Sapon. acetate	81	—	—	29
Durafil	—	46	—	29
Toromomen	—	56	—	25
Tenasco Reg.	39	43*	17	20
Tenasco 201	45	34*	6	20
Tenasco 301	39	35*	15	—
Tenasco 401	55	34	*ca.* 4	20
Tenasco 401-A	35	—	20	—
Tenasco 501	40	—	8.3	—
Super A	56	37	24	17
Super Super A	49	—	7	—

* Private communication from Dr. N. S. Wooding.
† Anhydro glucose units.

polarized light from a sodium lamp. The fiber was immersed in liquid mixtures of tricresyl phosphate ($n_D^{20} = 1.556$) and dibutyl phthalate ($n_D^{20} = 1.493$) until inspection of the Becke line and its movement when the microscope was moved from just out of focus above, to just out of focus below the fiber, indicated that the refractive index of the liquid and of the fiber were identical. The crenulated cross-section of ordinary viscose yarns and the existence of voids in super-yarns makes measurements difficult, as often more than one Becke line can be observed. The results are normally accurate and reproducible to 0.001 unit. Refractive indices were determined at 65% RH and 20° C.

Orientation from X-ray diffraction measurements. Sisson and Clark [5] have shown that the distribution of crystallites around the pencil of X-rays is related to the distribution of intensity around the (002) ring. They suggested a parameter:

$$O = \frac{R - L\ (002)}{R} \times 100$$

where R = radius of 002 reflection, L = length of arc of 002 reflection from equator to the point 50% intensity compared to equatorial intensity.

Another parameter, the orientation factor $f(x)$ [8, p. 255] was obtained from angular intensity distribution measurements. Since, for the samples studied, the angles were small and the distribution curves approximately Gaussian in shape, a simplified formula for $f(x)$ was used [4]:

$$f(x) = 1 - 1.65 \times 10^{-4} \{B^2(\tfrac{1}{2}) - \gamma^2(\tfrac{1}{2})\}$$

where $B(\frac{1}{2})$ and $\gamma(\frac{1}{2})$ are the corresponding half intensity angles for 101 and 101–002 doublet.

Results and Discussion

It is difficult to assess the importance of chain length to the physical properties of cellulose yarns, except in so far as it affects the products of closely related processes (Table II).

The figures given in Table II indicate the order of magnitude of the effects observed. Small variations from sample to sample of the same type of yarn are ignored and a rounded average figure quoted.

While in the Tenasco series the exceptional strength and fatigue properties of 401 could be associated with a higher average DP as well as with the absence of material below DP 300, the fact that superior properties were obtained with normal DP and DP distribution (Tenasco 501) suggests that the real answer (at least at the level of strength attained to date) must lie with the molecular configuration rather than DP.

It is doubtful whether any significant increase in crystallinity has accompanied improved properties in the Tenasco series (Table III). There is some evidence from X-ray diffraction measurements of an increase in crystallinity, but, on the other hand, crystallinity measurements based on density determinations fail to confirm this trend. This is also true in the Super A series.

However, when we examine the degree of perfection of the crystalline fraction as shown by the intensity ratio determination, we see in the Super A

TABLE IV. Relative Quantities of Material of Medium Order as Shown by Formylation

Yarn	Accessibilities at 4° C.	Accessibilities at 35° C.
Durafil	19	56
Saponified acetate	11	22
Textile	15	62
Tenasco Regular	27	77
Tenasco 201	23	79
Tenasco 301	23	75
Tenasco 401	27	80
Tenasco 401-a	29	80
Tenasco 501	19	81
Super A	32	68
Super Super A	23	71

TABLE V. Accessibilities as Measured by Moisture Regain and Water Imbibition

Yarn	Sorption ratio, moisture regain	Water imbibition
Textile	2.04	119
Durafil	1.86	82
Saponified acetate	1.50	49
Toromomen	1.82	73
Tenasco Regular	2.21	87
Tenasco 201	2.27	77
Tenasco 301	2.26	77
Tenasco 401	2.23	71
Tenasco 401-a	2.11	76
Tenasco 501	2.23	81
Super A	2.14	66
Super Super A	2.06	71

series a distinct lowering of the degree of crystallite perfection as properties improve. Again in the Tenasco series, there is a slight trend in this direction. One exception to this is Tenasco 301, which one can see from Table I was characterized by better tensile properties than Tenasco 201, but inferior fatigue resistance. Thus, there is some uncertainty as to whether this yarn constitutes progress from Tenasco 201, or is a retrograde step. Another apparent exception is Tenasco 401-a. Again good strength, but a slightly inferior fatigue resistance.

There is a growing realization today of the important effect of finish and surface characteristics on the performance of yarns in fatigue tests [14]. One has, therefore, to recognize that these secondary characteristics may have the effect of increasing the variability of tests and tend to obscure the intrinsic fatigue resistance of the fiber itself. All of the Tenasco yarns reported here were lubricated with substantially the same composition of finish.

TABLE VI. Orientation Measured from Optical and X-Ray Parameters

Sample	Birefringence at zero moisture cont.	$O=R-L(002)/R$	$f(x)$
Durafil	0.0542	—	0.9945
Saponified acetate	0.0526	—	0.9990
Toromomen	0.0487	—	0.9931
Textile	0.0280	87	—
Tenasco Regular	0.0370	91	0.9898
Tenasco 201	0.0419	92	0.9917
Tenasco 301	0.0421	92	—
Tenasco 401	0.0421	90	0.9942
Super 501	—	80	—
Super A	0.0409	91	—
Super Super A	0.0461	91	0.9982

The result of measuring crystalline length from levelling off DP measurements (Table III) has shown that there is apparently little difference in the over-all length of these regions.

There has apparently been little or no change in the characteristics of the sub-crystalline phase as shown by formylation accessibility measurements (Table IV). Much the same sorts of conclusion can be drawn from sorption ratio and water of imbibition data (Table V).

An interesting structural characteristic was revealed by the soda swelling measurements. By measuring the change in relaxed length upon immersing a fiber in progressively increasing strengths of sodium hydroxide, important differences were detected between the latest products and those spun by earlier processes. Our results are shown in Figure 1.

The maxima in the differential curves represent soda concentrations at which an increase in the rate of yarn contraction with increasing soda concentration is taking place. Such increases indicate that rearrangements triggered by the swelling power of soda are occurring. The development of a second peak at higher soda concentrations seems to be characteristic of the stronger yarns. This suggests that, as a result of processing conditions, these yarns are characterized by metastability in the higher-order fractions, and that ordering has been accomplished without crystallization into relatively stable structures.

It is interesting at this point to inquire as to the relative effectiveness of the stretching operation as shown by X-ray and birefringence measurements (Table VI). While there is a significant increase

in the X-ray orientation factor $f(x)$ in Tenasco 401 compared to Tenasco 201 and 301, there appears to be no parallel increase in birefringence.

Of great interest is the low crystallite orientation of Tenasco 401-A and Tenasco 501. The Tenasco 401-A diagram is characterized by a bimodal intensity distribution around the (002) diffraction ring, which one may speculate is caused by a preferred diversion of the axis of the crystallite domains which forms a cone around the fiber with an opening angle of about 16°. This type of behavior has been observed in "semi" drawn filaments of polyethylene and polyamides. Consequently, the extremely low value for the orientation parameter cannot be related to the values quoted for other yarns which do not show this behavior. Tenasco 501 is related to Tenasco 401-a, differing only in the higher stretch applied to produce Tenasco 501.

In the "A" series of yarns, a considerable increase in birefringence has accompanied the improvement in properties. It is thought that this increase reflects a high stretch, which was applied while the filaments were in a highly swollen state, permitting orientation of individual chain segments, which results in high orientation of what eventually becomes the non-crystalline part of the fiber.

A decrease in mobility caused by the increase in DP in the case of Tenasco 401 may account for the fact that the crystalline orientation has increased while the orientation of the amorphous regions has not. Here the ready formation of junction points has fixed the structure early in the spinning process. A similar effect may be a result of a very low gel swelling at stretching.

Summary

Summing up we concluded that:

1. We have not yet realized the full benefit of high DP cellulose because the strength of yarns

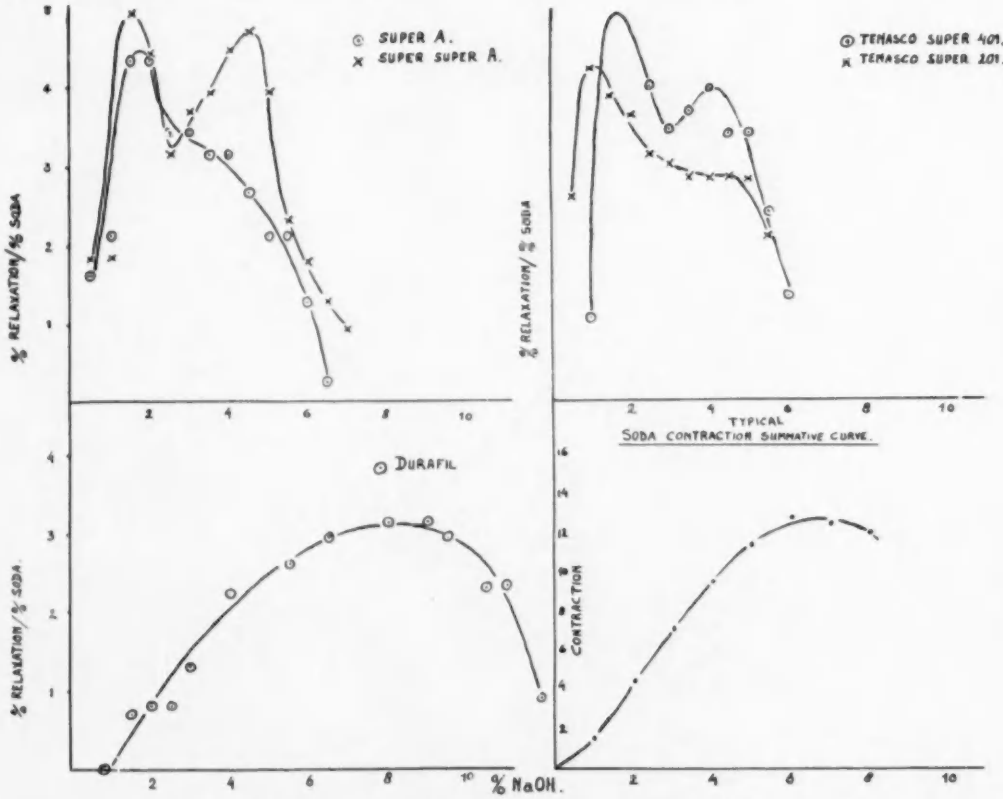

Fig. 1. Lateral order distribution from soda contraction.

at this time is dominated by other fine-structure characteristics.

2. A tendency to less crystallite perfection has accompanied the over-all improvement in properties.

3. The newer cellulosic tire yarns have a structural characteristic which can be detected as an unusual contractive response to the swelling induced by caustic soda.

4. We have been unable to discover any systematic trend in the structure of the amorphous phase. This must be due to the limitations imposed by the methods we employed, which were not subtle enough to resolve the sort of differences that must exist. It is very important at this time to develop methods which will give us information about the sub-crystalline phase. Without this development, the value of the fine-structure approach is very limited indeed.

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Cotton Fiber Maturity and Fineness: Both Predicted Separately, Accurately, and Rapidly

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Abstract

Both Causticaire fineness and Causticaire maturity of cotton fibers can be predicted separately, yet simultaneously, accurately, and rapidly. Only Micronaire readings, a conversion table, and the varietal identity are necessary for accurate predictions.

Introduction [2]

Cotton fiber maturity is generally considered to be the result of the inward thickening of the fiber as successive layers of cellulose are deposited during the stage of development after the fiber has attained its length [13, 16]. Therefore, it is generally considered that a thick-walled fiber is mature and a thin-walled fiber immature [2]. Fiber fineness or coarseness is defined as the weight per unit length or the linear density of the fiber [1]. The smaller the weight per unit length, the finer the fiber, and vice versa.

The above distinctions as to fineness and maturity imply that a fine fiber is immature and a coarse fiber is mature. For several years the Micronaire test was considered a measure of fineness, so the instrument was calibrated to show weight per unit length [3]. In more recent years, the Micronaire test has been recognized as a test of fineness and maturity in combination [15, 20, 21]. However, separate values are not provided for the two elements of quality that in combination affect the Micronaire reading.

Both fineness and maturity have been measured separately by the array method, a tedious and expensive procedure [1, 18]; moreover this method of testing these two properties has been deleted from the U. S. Department of Agriculture's list of fiber tests on a fee basis [19]. However, the array method is still used as a research tool. Succeeding the array method for determining maturity, a method often referred to in literature is the standard method or the random sample–sodium hydroxide swelling method [2]. This test, involving the use of a microscope or microprojector, slides, and a chemical, requires the visual classification of individual fibers. This method was too tedious and expensive to receive acceptance for large scale testing, and the results of the classification were not as accurate as desired. Webb and Burley [22] stated that the standard method for determining fiber maturity constituted the bottleneck in most cotton fiber research and testing programs. Carpenter [7] experimented with various ratios of fiber wall thickness to fiber lumen to be used as criteria of fiber maturity; but using various ratios did not appear to provide sufficient improvement over the ratio already in use in the standard method.

Burley and Bartmess [5, 6], and later Webb and Burley [22], reported that the development of the Causticaire method for evaluating both maturity and fineness constituted a notable step forward in fiber technology. The Causticaire method is, in principle and operation, unique in that only a combination of Micronaire readings for lint cotton (untreated) and the same cotton treated with sodium hydroxide (40 Tw.) is required for deriving the two measures. The Causticaire method proved to be a more accurate and practical test of fiber maturity than the standard maturity test; with no extra work, except a calculation, the Causticaire fineness value can also be obtained. Practically no personal error is involved in the method [10].

[1] One of the cotton ginning research laboratories of Agricultural Engineering Research Division, Agricultural Research Service, United States Department of Agriculture.

[2] Mention of commercial products in this publication is for identification only and does not imply endorsement by the U. S. Department of Agriculture.

Webb and Burley [22] reported that the Causticaire method furnished maturity values possessing significantly more relationship to nep count of card web, yarn appearance, and yarn strength than did either percentage of mature fibers (standard method) or immaturity ratio (Arealometer). The Arealometer proved to be somewhat better in those respects than the standard maturity test, but not as good as the Causticaire maturity measure. These workers also found a very high correlation (+ 0.976) between Causticaire fineness and the array method fineness.

Gaus and Burley [10] reported the development of mechanical batch processing of test samples for handling larger numbers of samples for the Causticaire test. Lee and Hernandez [12] compared three types of air permeability instruments for measuring fineness. They concluded, on the basis of their studies and considering the time required for tests and ease of operation, that the Micronaire satisfied the need for a method of determining fiber fineness at that time. There is now on the market another air permeability instrument for measuring fiber fineness—the Fibronaire.

Inasmuch as fineness and immaturity are measured in combination in the usual Micronaire test, the question arises as to the relative significance of each in its effect on the Micronaire reading. Superficially, it might seem that a low Micronaire reading would ordinarily denote both immaturity (lack of cellulose development) and fineness (low weight per unit length) and that a high Micronaire reading would denote both maturity and coarseness. However, it also seems possible that a fine fiber with an inherently small fiber perimeter could have a well developed cell wall and consequently be both fine and mature; also, a coarse fiber with a large perimeter might have a poorly developed cell wall and be both coarse and immature. Such possibilities might arise in comparing varieties and especially in comparing species.

A survey of 497 cotton spinning plants showed that in 1958 65% of the firms owned fineness testing instruments such as the Micronaire, but only 15% owned maturity testing instruments [9]. This is interpreted to be a result of the relative time and expense involved in obtaining the two tests and is not interpreted to be a result of the relative importance of the two properties. Fiber maturity is an important factor affecting the appearance of yarns and fabrics; immature fibers contribute to the formation of neps; cottons differing in degree of maturity do not dye uniformly; and fiber maturity is a desirable characteristic from the standpoint of low picker and card waste [17].

Various cotton-research workers and segments of the cotton industry have expressed a need for a rapid, simple, inexpensive test for fiber maturity. Therefore, the author and co-workers have attacked the problem and attempted to fulfill the objective.

Experiments and Results

Preliminary work [8] developed a quick, simple, and economical test of the degree of cotton fiber maturity. Cotton fiber specimens of constant weight (50 grains) were tested in a Micronaire having a cylinder and plunger with a removable $\frac{1}{2}$-in. spacer to change the volume of the cylinder from standard to 150% of the standard. Micronaire readings were higher when the volume of the cylinder was increased. With 57 samples of American upland or *Gossypium hirsutum* species, including several varieties of southwestern irrigated cottons, differences in Micronaire readings for the same specimens at the two chamber volumes were found to correlate highly with Causticaire maturity ($r = +0.90$).

Sundaran and Iyengar [14] in India reported similar results. Using a $\frac{3}{8}$-in. spacer and several species of cotton, they found a lower correlation, +0.80, between the differences in readings with and without the spacer and maturity coefficient. Their maturity test appears to be similar to the standard or random sample–sodium hydroxide swelling method [2]. When they grouped their samples according to species, the cottons belonging to *G. herbaceum* provided an improved correlation of +0.86.

The preliminary studies by Chapman and Staten [8] were expanded to include $\frac{1}{2}$-, $\frac{3}{8}$-, and $\frac{1}{4}$-in. spacers with a Model No. 70600 Micronaire equipped with a USDA curvilinear scale for upland cottons. Tests of 81 samples of upland cotton showed that not only were differences in Micronaire readings with and without each spacer correlated highly with Causticaire maturity, but the mere readings with each spacer alone (that is, without computing differences between readings at the standard and increased cylinder volumes) were also highly, and approximately equally, correlated with Causticaire maturity. The thinner spacers provided more readings within the range of the Micronaire upland cotton curvilinear scale than did the $\frac{1}{2}$-in. spacer.

In addition, Micronaire readings at standard volume (that is, without any spacer) compared very favorably with readings when spacers were used. Therefore, the use of spacers was discontinued. Both linear and curvilinear correlations were calculated, and the curvilinear found to be higher in some instances. Both linear and curvilinear correlation coefficients for five methods of predicting maturity, each compared with Causticaire maturity, were as follows:

Method	Linear	Curvilinear
1. ½-in. spacer minus regular Micronaire reading	+0.90	+0.91
2. ½-in. spacer alone	+0.92	+0.93
3. ¾-in. spacer minus regular Micronaire reading	+0.92	+0.93
4. ¾-in. spacer alone	+0.92	+0.95
5. Micronaire reading with no spacer	+0.92	+0.95

The ¾-in. spacer alone and the Micronaire reading without spacer (Methods 4 and 5) provided the two highest curvilinear correlations, +0.95. Obviously the elimination of the spacer further simplified the technique. Therefore, our succeeding research on predicting maturity was concentrated on the use of Micronaire readings without spacers.

Material published by Agricultural Marketing Service, USDA, provided data on Micronaire readings, Causticaire fineness, and Causticaire maturity for as many as 33 upland varieties and one American-Egyptian variety (a total of 1,231 samples of upland cotton) representing various areas of growth for three years [15, 20, 21].

In the comparison of Micronaire readings with Causticaire maturity indexes, the plotted points of the measurements from 1,231 upland samples and 48 American-Egyptian samples gave curvilinear regression lines. The curvilinear correlations for all upland samples, for the American-Egyptian samples, and for each of six selected upland varieties were slightly higher than the respective linear correlations, and the maturity predicting formulas, on which the conversion table is based, are in relation to curvilinearity (Table I).

In predicting Causticaire fineness from Micronaire readings, the curvilinear correlations were usually slightly higher than the linear correlations. As with the maturity predicting formulas, the fineness predicting formulas were based on curvilinearity. For predicting both maturity and fineness from the Micronaire reading, therefore, the conversion table is based only on the curvilinear regression lines.

TABLE I. Conversion Table for Predicting Causticaire Fineness and Maturity from Micronaire Readings.
(Causticaire fineness (F) and maturity (M) readings for varieties listed)

Micronaire reading*	Acala 4-42		Arizona 44		Acala 1517C		Lankart		Deltapine		Coker		All 33 upland varieties		Pima S-1	
	F	*M*	*F*	*M*	*F*	*M*	*F*	*M*	*F*	*M*	*F*	*M*	*F*	*M*	*F*	*M*
5.5	—	—	—	—	—	—	—	—	—	—	—	—	5.4	81	—	
5.4	—	—	—	—	—	—	—	—	5.3	82	—	—	5.3	81	—	—
5.3	—	—	—	—	—	—	—	—	5.2	82	—	—	5.2	81	—	—
5.2	—	—	—	—	—	—	5.2	80	5.1	81	—	—	5.2	81	—	—
5.1	—	—	—	—	—	—	5.1	80	5.0	81	—	—	5.1	81	—	—
5.0	4.9	81	—	—	—	—	5.0	80	5.0	81	—	—	5.0	81	—	—
4.9	4.8	81	—	—	—	—	5.0	80	4.9	81	4.8	81	4.9	81	—	
4.8	4.7	81	—	—	—	—	4.9	79	4.8	81	4.7	81	4.8	80	—	
4.7	4.7	80	4.5	81	—	—	4.8	79	4.7	80	4.7	81	4.7	80	—	—
4.6	4.6	80	4.5	80	—	—	4.8	79	4.6	80	4.6	80	4.6	80	—	—
4.5	4.5	79	4.4	80	—	—	4.7	78	4.5	80	4.5	80	4.6	79	—	
4.4	4.4	79	4.3	80	—	—	4.6	78	4.5	79	4.4	79	4.5	79	—	—
4.3	4.3	78	4.2	79	—	—	4.5	77	4.4	78	4.4	78	4.4	78	—	—
4.2	4.2	78	4.2	79	4.1	79	4.4	77	4.3	78	4.3	78	4.3	78	3.6	83
4.1	4.2	77	4.1	78	4.0	79	4.4	76	4.2	77	4.2	77	4.2	77	3.5	82
4.0	4.1	77	4.0	78	4.0	78	4.3	75	4.1	76	4.1	76	4.1	77	3.5	81
3.9	4.0	76	3.9	77	3.9	77	4.2	75	4.0	76	4.0	76	4.0	76	3.4	80
3.8	3.9	75	3.8	76	3.8	76	4.1	74	3.9	75	3.9	75	3.9	75	3.4	79
3.7	3.8	74	3.7	75	3.7	76	4.0	73	3.8	74	3.8	74	3.8	74	3.3	78
3.6	3.7	74	3.6	74	3.6	75	3.9	72	3.7	73	3.7	73	3.7	73	3.2	78
3.5	3.7	73	3.5	73	3.5	74	3.8	71	3.6	72	3.7	72	3.6	72	3.2	77
3.4	3.6	72	3.4	72	3.4	73	3.7	70	3.5	71	3.6	72	3.5	71	3.1	76
3.3	3.5	71	3.3	71	3.3	72	3.6	69	3.4	70	3.5	71	3.5	70	3.0	76
3.2	3.4	70	3.1	70	3.2	71	3.5	68	3.3	69	3.4	70	3.4	69	2.9	75
3.1	—	—	—	—	3.1	70	3.4	66	3.2	68	3.2	69	3.3	68	—	—
3.0	—	—	—	—	3.0	69	3.3	65	3.1	66	3.1	68	3.2	67	—	—
2.9	—	—	—	—	2.9	67	3.2	64	2.9	65	—	—	3.1	65	—	—
2.8	—	—	—	—	2.8	66	3.1	62	2.8	64	—	—	3.0	64	—	—
2.7	—	—	—	—	—	—	3.0	61	2.7	62	—	—	2.9	62	—	—
2.6	—	—	—	—	—	—	2.9	60	2.6	61	—	—	2.8	61	—	—
2.5	—	—	—	—	—	—	—	—	—	—	—	—	2.7	59	—	—
Number of samples used	84	84	60	60	83	83	108	108	424	424	215	215	1,231	1,231	48	48
Curvilinear correlation	+0.84	+0.87	+0.95	+0.95	+0.92	+0.94	+0.92	+0.96	+0.92	+0.90	+0.90	+0.91	+0.92	+0.92	+0.82	+0.86

* "USDA Curvilinear Scale for Upland Cottons" used for all Micronaire readings with all cottons including Pima S-1.
Source: Southwestern Cotton Ginning Research Laboratory, AERD, ARS, USDA, and data from Annual Cotton Quality Survey, AMS, USDA.

More important than the correlations shown at the bottom of the table are the differences in the predicting formulas for different cottons. For example, in the conversion table, the same Micronaire reading of 4.0 for Acala 1517C and Lankart varieties indicates that the former is relatively finer and more mature. At identical Micronaire readings, more pronounced differences in fineness and maturity are noted when comparing the two species, or the American-Egyptian variety Pima S-1 with the American upland varieties.

Where $\hat{Y}$ = predicted Causticaire *fineness* and X = Micronaire reading, the *fineness* predicting formulas for different varieties are as follows:

Arizona 44	$\hat{Y} = -0.545 + [1.612\ (X-2)] - [0.175\ (X-2)^2] + 2$
Deltapine	$\hat{Y} = -0.122 + [1.254\ (X-2)] - [0.075\ (X-2)^2] + 2$
Coker	$\hat{Y} = -0.030 + [1.280\ (X-2)] - [0.106\ (X-2)^2] + 2$
Lankart	$\hat{Y} = 0.134 + [1.278\ (X-2)] - [0.103\ (X-2)^2] + 2$
Acala 4–42	$\hat{Y} = 0.483 + [0.759\ (X-2)] + [0.018\ (X-2)^2] + 2$
Acala 1517C	$\hat{Y} = -0.260 + [1.468\ (X-2)] - [0.181\ (X-2)^2] + 2$
All 33 upland varieties	$\hat{Y} = 0.184 + [1.012\ (X-2)] - [0.026\ (X-2)^2] + 2$
Pima S-1	$\hat{Y} = -0.352 + [1.274\ (X-2)] - [0.178\ (X-2)^2] + 2$

Where $\hat{Y}$ = predicted Causticaire *maturity* and X = Micronaire reading, the *maturity* predicting formulas for different varieties are as follows:

Arizona 44	$\hat{Y} = 1.727 + [19.100\ (X-2)] - [3.093\ (X-2)^2] + 50$
Deltapine	$\hat{Y} = 1.030 + [18.081\ (X-2)] - [2.676\ (X-2)^2] + 50$
Coker	$\hat{Y} = 5.110 + [14.204\ (X-2)] - [1.764\ (X-2)^2] + 50$
Lankart	$\hat{Y} = -0.682 + [18.701\ (X-2)] - [2.859\ (X-2)^2] + 50$
Acala 4–42	$\hat{Y} = 4.652 + [15.339\ (X-2)] - [2.172\ (X-2)^2] + 50$
Acala 1517C	$\hat{Y} = 4.798 + [16.060\ (X-2)] - [2.263\ (X-2)^2] + 50$
All 33 upland varieties	$\hat{Y} = 0.739 + [18.748\ (X-2)] - [2.916\ (X-2)^2] + 50$
Pima S-1	$\hat{Y} = 25.128 - [4.052\ (X-2)] + [3.536\ (X-2)^2] + 50$

Since the Micronaire reading is acknowledged to measure both fineness and maturity in combination [15, 20, 21], the logic in predicting the two properties separately from one measurement might be questioned on the basis that the relationship between fineness and maturity may be constant. However, when the Causticaire fineness and Causticaire maturity relationship was analyzed with the 1,231 upland samples, the curvilinear correlation, much higher than the linear correlation, was only +0.75. This indicates that there is some relationship between fineness and maturity; in fact, one is explained to the extent of 56% by the other. The remaining unexplained variation shows a degree of independence between fineness and maturity, and this indicates that one of the Causticaire measurements cannot be used to predict the other accurately. And yet, our results show that both fineness and maturity can be predicted simultaneously, quickly, and accurately with the Micronaire reading and conversion table, when the variety is known.

Fineness and maturity can be predicted by the method herein reported with precision adequate for industrial usage.

Summary and Conclusions

A method of predicting fineness and maturity of cotton fibers is described. The principle of varying the volume of the compression cylinder was adapted for use in the Micronaire by using a spacer; the difference between the two readings on the same cotton specimen when volumes in the Micronaire cylinder were varied correlated highly with Causticaire maturity. Direct Micronaire readings with spacers of different thicknesses and with no spacer were also made. Direct readings were highly correlated with both Causticaire fineness and Causticaire maturity values; some of the best correlations were obtained when the standard volume of the Micronaire cylinder was used.

Both Causticaire fineness and Causticaire maturity can be rapidly predicted at the same time and with satisfactory accuracy on known varieties of upland

and one variety of American-Egyptian cotton. A conversion table shows the relation of Micronaire readings at standard volume of the cylinder to both Causticaire fineness and maturity of several upland varieties and one American-Egyptian variety. With the USDA Curvilinear Scale for Upland Cotton and the conversion table presented herein, the Micronaire can be used to predict cotton fiber fineness and maturity with precision adequate for industrial usage.

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Contribution of Swelling to Water-Resistant Cotton Fabrics[1]:

Effects of Maturity of Cotton, Cloth Construction, and Finishing Processes

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Abstract

A summary of a comprehensive study of the manufacture and finishing of swelling-type water-resistant cotton fabrics of medium weight is presented. These are fabrics which stop the passage of water by the swelling of their constituent fibers. Such stoppage depends upon a zone of very high density flatwise through the fabric. Of many fabrics produced, a few were of swelling type in the grey, but only one after finishing.

Variables which are usually given less consideration, had most attention, *viz.*, maturity, and use of very immature cottons; effects of processing the yarn before weaving; and effects of increasing the tightness of fabrics by adding picks up to 36% more than normal. The fabrics were finished in a pilot plant, and an unusual study was made of the effects of successive steps in finishing on air and water resistance.

Unique fabrics produced showed unusual properties, especially strength and thickness.

Fabrics were evaluated for closing by methods intended to exclude water resistance from other sources than swelling. Many special tests showed that swelling capacity was reduced by finishing, to a greater extent with immature than with mature cottons. The air spaces in dense, grey fabrics of very immature cotton constitute capillary systems of unusually fine pores, especially resistant to the passage of air or water. This advantage over mature cotton is largely offset, however, because the immature cotton loses 4–5% more noncellulosic material when scoured, which leaves more space to fill by swelling. Cottons of average maturity, and from fine to average in fineness, are preferable.

Entrapped air in partially swollen fabrics contributed to water resistance beyond the effect of air in ordinary water-repellent goods. This was observed especially in samples swollen in water vapor and may add to the resistance of a fabric in service if exposed to a very humid atmosphere.

Introduction

Cotton fabrics can be so constructed that, when wet, their fibers will swell and stop the passage of water, but such fabrics can be made only under very special conditions. Such fabrics, designated for convenience as of "swelling type," would be self-sealing and water-tight. Swelling-type fabrics have long been of considerable interest, but it appears from results to be described that swelling has added less than has been thought in the past to the water resistance of many cotton fabrics in which it was supposed to have been an important factor. Cotton has been less successful in this field than linen although considered at various times for use in clothing, water bags and tanks, etc. Now, more of the essential factors involved are believed to have been recognized, and cotton fabrics have been made which seem to justify the designation "swelling type."

Some of the results of this investigation may be of broader interest. These include properties of comparable yarns and fabrics made from cottons varying widely in maturity and fineness; the high

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resistance to air flow achieved with cotton of extreme immaturity; and physical properties of fabrics in a series where the picks/in. vary from normal up to 36% additional picks/in. Fabrics of some of these constructions had apparently not previously been made, and they showed unexpected differences in strength and thickness.

Other data are more closely related to swelling-type fabrics; these include the effects of separate steps in finishing upon the air and water resistance of very closely woven fabrics. Finally, a seemingly unfamiliar effect of air enclosed within the fabrics was noted which may have almost as significant an effect on stopping water as does fiber swelling.

All features of this work have been discussed in detail in five papers recently published [1, 2, 3, 9, 10]. The present paper is a summary based on those original papers.

The results presented were obtained from pilot plant manufacturing and finishing, and from laboratory evaluation. A few opinions, believed justified by the experimental work, are also offered because it was not possible to complete all aspects of the research.

A review of the limited literature on swelling-type fabrics in one of the original publications [3, p. 1] hardly needs to be repeated.

Much of the present work was done during close contact with the Quartermaster Corps and was undertaken initially as a study of the swelling of cotton. Since no applicable measure of the effects of swelling was found unless the cotton was in the form of yarn or cloth, the investigation was carried through to finished goods.

Style of Experimental Fabrics

The oxford weave was adopted as the main construction because it appeared to be of most general interest. The two warp ends laid together in this style correspond roughly with one wider, flatter warp end. In the piece, the warp has a high crimp and the filling very little; the warp passes through the fabric the maximum possible number of times for a given filling count. In the ideal swelling-type fabric, there would be a plane of maximum density flatwise through the center as indicated by photomicrographs of oxford fabrics [3, p. 10–13]. In reality, it is a zone of maximum density of appreciable thickness, rather than a plane.

The fibers and yarns in such a structure are intended to swell against each other and to close interspace both within and between the yarns, with a minimum of deflection from the theoretical plane. Plain weaves may also be suitable; but in constructions such as sateens, floating yarns would swell ineffectively along the surface of the cloth and not contribute to closing.

Selection of Cotton

Greater capacity to impede the passage of water by swelling in a restricted space was shown by immature than by mature cotton. For example, comparable yarns made from cottons of 44% and 92% maturity allowed seepages of 1.0 and 11.8 ml. of water, respectively, in an orifice test [11]. The lower seepage resulted from the greater closing capacity of the immature cotton; this was confirmed after the yarns were made into comparable fabrics. The results indicate that the immature cotton swelled more than the mature cotton, but fineness of fiber adds a complication attributable to differences in fineness of the capillary systems among the fibers in the two fabrics. This was most simply shown by the permeability to air, which was lower in either grey or finished samples of the immature-cotton fabric than in the mature. In these fabrics the capillary spaces between fibers can be assumed to differ in size in accordance with the size of the fibers, 5.6 and 3.6 μg./in. linear density, respectively. The capillaries of both became still finer, but to unknown degrees, when the fabrics became wet and swollen.

That fineness of fiber alone can cause decrease of flow of liquid was shown in two ways by orifice tests [11]. There was less flow through a fine, nonswelling fiber, Vinyon, than through coarse Vinyon, and less flow of a nonswelling liquid through immature (fine) cotton than through mature (coarse) cotton. Since, also, seepage of water was retarded relatively more than seepage of the nonswelling liquids by immature as compared with mature cotton, and by an amount apparently greater than accounted for by the difference in capillary size [11], it follows that the immature cotton had greater closing capacity by swelling. Other evidence that immature cotton swells more than mature will be found in Table V and in the original discussion [1].

Selection and Improvement of Yarn

The two main considerations in selecting yarn for swelling-type fabrics were yarn construction and the effects of physical and chemical treatments of the yarn on fabric construction and closing capacity.

Yarn construction depended upon the cotton. American cottons, readily available in quantity, were of most interest. Since combing would be undesirable in any large scale end use, and since some of the experimental cottons could not be combed, only a few fabrics were made from combed yarn. Rather, nearly all were made from carded yarns of low to medium twist. There was slight, if any, advantage in using combed rather than carded yarns to achieve closing by swelling, according to comparisons by the orifice test.

Most of the yarns were twisted into two ply in the direction opposite to that of the twist in the singles. Tests with a few singles filling yarns showed only slight difference in over-all performance as compared with equivalent 2-ply yarns in similar fabrics. It appeared from orifice tests on yarns that there would be very little difference in swelling-type fabrics arising from any difference in twist within the practical range for ordinary American cottons. Further, allowable differences in twist would have little effect in tight fabrics, where swelling of the cotton would be affected more directly by the density of the fabric than by that of the yarns entering into it.

Yarn may be processed before weaving to adapt it for making a more dense fabric and to reduce the opening effect of finishing. Mercerization under tension is probably the most practical process for making yarn more compact and of lower elongation as a step toward achieving tighter fabrics, but the yarn would have the effect of being finer. An improvement could also be made by scouring, preferably under tension, before weaving. This would remove noncellulosic constituents at once and so not only allow a tighter fabric to be woven, but also avoid subsequent removal of material with its tendency to make the fabric more open in texture. To obtain the full advantage of such yarn treatments in the improvement of a given fabric, heavier yarn might be needed, or more warp ends or filling picks.

Treatment of yarn by adding a swellable material that would not dissolve in water helped solve the problem of producing a swelling-type unlined cotton firehose [4]. The yarn carried this additional material into the fabric as a permanent part of the structure, where it not only filled a small percentage of the space but aided in closing the fabric by swelling into some of the most critical remaining space.

All warps in this study, with the exceptions to be noted, were employed without sizing. This omission offers several advantages: 1. The effects of using different cottons, unchanged from their natural state except by mechanical processing, can be compared. 2. Fabrics of different construction can be compared without having to take into account the effect of added size, wet treatment to remove size, or residual size. 3. Uncertainty as to the amount of additional interfiber and interyarn space which results from the removal of size and which is to be closed by swelling is thus avoided.

Weaving Tighter Fabrics

To make the dense fabrics required it was necessary to crowd more yarn into the critical zone in the center of the fabric. It was not practical to put in

TABLE I. Fiber and Yarn Properties

Fabric number	Variety of cotton	Maturity (caustic soda), %	Fineness (by weight), microg./in.	Yarn numbers	Twist multiplier		Seepage in orifice test, ml./10 min.
					Singles	Ply	
110, 111	Acala 1517 W	85	3.3	Warp 34.9/2	3.5	4.2	5.4
				Filling 21.8/2	3.5	3.8	5.1
101–105	Acala 1517 W	74	3.2	Warp 34.8/2	3.5	4.2	5.0
				Filling 23.0/2	3.5	3.8	5.0
106–107	Acala 1517 W	58	2.5	Warp 35.2/2	3.5	4.2	0.7
				Filling 21.7/2	3.5	3.8	0.5
114–118	Deltapine	85	4.4	Warp 29.6/2	4.6	5.1	9.4
				Filling 30.0/2	4.6	3.3	10.1
119–123	"Sike" (unknown)	30	2.6	Warp 30.6/2	4.6	5.1	0.3
				Filling 31.2/2	4.6	3.3	0.1

more warp ends so this part of the problem was solved in the Cotton Mechanical Laboratory (SRRL) with their special high pickage loom attachment [6]. By its aid, up to 36% more filling threads per inch than usual were put into 8–10 oz. fabrics. Since all the warp threads in an oxford (or plain weave) fabric pass through the central plane once more for each added pick, there were great increases in tightness with only moderate increases in fabric weights.

Cover factors of 46 to 51 were attained, but in identical fabric constructions of equal cover factor but made of different cottons there was sometimes considerable difference in water resistance. Fabrics like most of these had apparently never been made before. Hence their physical properties were reported [2, 10], including a few unusual features described below.

There seems to be little chance during the finishing of the fabrics to improve their closure by swelling except by the avoidance of harmful practices.

Experimental Fabrics

Only a sufficient number of experimental fabrics are reported on here to show that it is possible to make swelling-type fabrics, and to indicate some of the conditions that are favorable or unfavorable. Many additional fabrics are described in the original publications.

The cottons used differed from 30% to 92% in maturity, and from 2.6 to 5.6 μg./in. in fineness, which was mainly dependent upon maturity. The finest cotton was the most immature, and one of the coarsest was the most mature.

Most of the fabrics were based on a 9-oz. oxford construction. They were made in pairs, or in larger groups, to allow comparisons of results as one or more of the most important variables were changed. Each fabric was made entirely from one cotton, with 2-ply warp and usually with 2-ply filling. The fabrics made in a series of pickages from a given cotton were all woven consecutively with the same warp.

Fabrics Made from Treated Yarns

Of the numerous fabrics made from treated yarns, none could be considered to be of swelling type so they are not being reported here in detail, although fully described in one of the original publications [2]. Most of these fabrics were made from fine cottons, with a few from a cotton of "average" fineness and of about 11% higher maturity. Some were of combed and some of carded yarns; and some with singles and others with comparable plied yarns in the filling.

Mercerization of the yarns caused changes in their diameters and compactness, which made the fabrics slightly more open in texture (shown by air flow) when there were no more ends or picks than in the comparable unmercerized-cotton fabrics. However, the fabrics made from mercerized yarns leaked somewhat less when preswollen [2]. This is taken to demonstrate greater swelling capacity of mercerized than of unmercerized cotton, shown also by orifice tests on yarn, and by centrifuge retentions of water in fabrics [2, p. 24, Tables IV and V]. The less mature and slightly finer cotton gave somewhat better results than the other, and was a little better still when the yarns were mercerized.

A few experiments with Ceglin [4] (alkali-soluble hydroxy ethyl cellulose) in fabrics of ordinary construction have been described [2, p. 19]. This swellable material was added and could no doubt give outstanding closure by swelling of fabrics for any special purpose for which it could be used. Since it acted as a size, the results indicate that a suitable warp size, not removed from the goods in finishing, could contribute to closing by its mere presence within the fabric, as well as by swelling.

Work with treated yarns was not carried up to the production of fabrics that actually closed by swelling, largely because of the difficulties and expense of practical yarn processing. The opinion may, however, be expressed that to obtain the best possible fabrics to close by swelling, one should include trials of yarns scoured and mercerized under tension. Although that might normally be considered impractical, such treatments of yarn could be expected to help in making the highest quality of fabrics of swelling type.

Fabrics Made from Grey Yarns

Descriptions and test data are shown in Tables I, II, and III for the experimental fabrics which were considered to be of swelling-type, for others which approached that quality, and for a few "control" fabrics. More extensive data on these and other fabrics are given in the original publications.

[4] Mention of company or trade names is for information and convenience only and does not imply endorsement by the U. S. Department of Agriculture over firms or products not mentioned.

The test to establish closing by swelling which seems most significant is that for amount of leakage of water under hydrostatic pressure through preswollen (prewet) samples (Appendix). Its results were usually confirmed by low values of leakage through preswollen samples in the Bundesmann [4] test, and low values in the rain test. A high hydrostatic pressure in the conventional Suter [4] test, and low air permeability have also been significant properties of the swelling-type fabrics described.

The experimental fabrics in one group (Table II) were made from relatively fine cottons. There were great improvements in both air and water resistance with 28–34% additional picks/in., although increases in weight per square yard were only 13–17%. There was a distinct tendency for air and water resistance to improve with fineness and with decrease in maturity of the three cottons used.

Fabrics No. 103, 104, 105, 107, and 111 (Table II) would probably all qualify in the grey as of swelling-type. They were all especially low in hydrostatic leakage when preswollen; were especially impervious to air; and rated very high in the regular hydrostatic test. After finishing, however, only Nos. 103, 104, and 105, all plain weave, came close to being of swelling-type, and of these, No. 105 may have been the only fabric of true swelling type after finishing produced in the entire research project. This particular fabric probably had an advantage in being made from rather fine cotton of average maturity. The plain weave was of doubtful advantage because other fabrics of the same group in oxford and plain weaves, but otherwise similar, behaved alike in the usual tests.

In the fabrics just described, fineness due to immaturity was an apparent advantage, but work with a much more immature cotton showed that one should not go too far in this direction. Fabrics were made from a very fine cotton of only 30% maturity in a series with increasing numbers of picks up to 30% more than normal, and a comparable series was made from a rather coarse cotton of 85% maturity. In these two groups the maximum increases in weight per square yard were only 11% and 9%, respectively. The more significant of the test results are given in Table III. There were progressive decreases in air permeability of the grey fabrics as number of picks increased, decreases in leakage of water in the tests to evaluate swelling, and pronounced increases in hydrostatic head required to cause leakage. The immature (finer) cotton made tighter fabrics. Of the unfinished (grey) fabrics, No. 118 made from the coarser cotton approached swelling type; and Nos. 121, 122, and 123 made from the finer cotton would probably qualify as such. The extreme improvement is represented by the difference between 1173 and 0.1 ml. leakage, brought about by the combined effect of the difference in the nature of the cotton and the increase in number of picks per inch.

It was quite different with the finished fabrics. Those made from the mature cotton showed regular

TABLE II. Air and Water Resistance of Fabrics of Oxford and Plain Weaves (Acala 1517W)

Fabric number	Maturity of cotton, %	Type of weave	Construction		Air permeability		Hydrostatic pressure head, cm.	Hydrostatic leakage (prewet samples, 86 cm. head), ml./5 min.	Bundesmann penetration (prewet samples), ml./20 min.	Rain test (8-ft. head, sample 6″ from nozzle), g./20 min.
			Warp ends	Filling picks	Permeometer, ft.³/min./ft.²	Densometer, (time/300 cm.³), min:sec				
A. Grey										
110	85	Oxford	124	53	0.72	11:26	69	364	2.8	5.16
111	85	Oxford	126	68	0.21	42:21	113	7.9	0.0	0.52
101	74	Plain	122	54	0.93	10:48	73	382	12	Over 10
103	74	Plain	122	68	0.00	49:54	143	1.7	0.0	0.48
104	74	Plain	122	69	0.00	53:06	159	0.1	0.0	0.44
105	74	Plain	122	71	0.00	58:30	161	0.0	0.0	0.44
106	58	Oxford	124	52	0.27	28:38	61	90	0.2	1.65
107	58	Oxford	124	68	0.00	122:00	123	0.1	0.0	0.54
B. Finished										
110	85	Oxford	128	53	0.87	10:28	51	2449	17	2.89
111	85	Oxford	130	67	0.30	30:17	69	122	0.0	0.47
101	74	Plain	124	53	0.90	8:27	62	1900	14	3.66
103	74	Plain	122	69	0.15	29:29	90	27	0.0	0.36
104	74	Plain	122	70	0.18	33:46	93	18	0.0	0.42
105	74	Plain	122	71	0.18	35:28	98	9.2	0.0	0.35
106	58	Oxford	130	51	0.93	9:14	46	2869	8.1	2.39
107	58	Oxford	130	66	0.90	10:48	53	339	0.0	0.98

TABLE III. Air and Water Resistance of Oxford Fabrics

Fabric number and kind of cotton	Maturity of cotton, %	Construction		Air permeability		Hydrostatic pressure head, cm.	Hydrostatic leakage (prewet, 86 cm. head), ml./5 min.	Bundesmann penetration (prewet), ml./20 min.	Rain test (8-ft. head, 6″ from nozzle), g./20 min.
		Warp ends	Filling picks	Permeometer, ft.³/min./ft.²	Densometer (time/300 cm.³), min:sec				
A. Grey									
114 Deltapine	85	124	56	0.87	9:03	65	1173	5.6	over 10
118 Deltapine	85	124	72	0.09	32:49	95	20	0.0	0.62
119 "Sike"	30	124	56	0.21	36:49	88	29	0.0	0.82
121 "Sike"	30	124	64	0.00	58:08	108	3.5	0.1	0.47
122 "Sike"	30	124	68	0.00	78:00	114	1.0	0.0	0.45
123 "Sike"	30	125	73	0.00	115:00	116	0.1	0.0	0.32
B. Finished									
114 Deltapine	85	128	56	0.87	9:42	55	2186	9.3	2.69
118 Deltapine	85	130	70	0.15	28:04	74	126	0.0	0.45
119 "Sike"	30	130	56	0.57	11:24	51	1962	5.2	1.10
121 "Sike"	30	130	63	0.57	15:23	52	772	2.4	0.66
122 "Sike"	30	130	65	0.51	15:23	52	509	0.6	0.57
123 "Sike"	30	130	71	0.57	16:13	53	176	0.1	0.44

improvement with increase in picks per inch, but greater leakages than when tested before finishing. The fabrics made from the immature cotton were more water-resistant at the two lowest pickages, but were less resistant than those of mature cotton at the three highest pickages. None of these finished fabrics were considered to qualify as of swelling type.

Yarns and Fabrics of Unusual Properties

Yarns made from cottons which were much more immature than usual, fabrics made from these yarns, and fabrics of extra high pickage may be of interest aside from water resistance because of some unusual physical properties. Many details are given in the original publications, and a few examples below.

Yarns made from cottons of 30–58% maturity were only 7% to 20% weaker than corresponding mature-cotton yarns, and had about one-fourth greater elongation. Fabrics made from cottons of 30% and of 85% maturity did not differ greatly in strength, elongation, or tear tests. Since immature cottons may be very different from one another, such results are not necessarily general.

A striking example of effects obtained with extra high pickage is shown in a series of plain weave fabrics, Nos. 101 to 105 (Table II). Warp strength decreased by 9% while filling strength increased by 64% upon the insertion of 31.5% more picks, but with a gain of weight of only 16.7%. The series started with a grey cloth 15% weaker in the filling than in the warp direction, and ended with the filling 52% stronger. Another striking difference was a decrease in thickness of 3% or 4% in spite of the increase in weight.

A novel self-cooling water bag which did not wet through in use was made from one of the fabrics but is not described further here although it may be of interest to some [10, p. 42].

Special Study of Finishing

Methods of Finishing

The commercial finishing of fabrics of the type and weight under discussion has included desizing, scouring in open width, mercerizing, dyeing, water repellency treatment, Sanforizing,[4] and calendering.

Most of the finishing of the experimental fabrics was limited to scouring, dyeing, and treatment with a durable water repellent [10, p. 42]. Desizing was not necessary. Fabrics were scoured by boiling twice on a jig in baths consisting essentially of 2% solutions of caustic soda. The cloth was vat dyed on a jig to an olive drab shade. For water repellency, the cloth was treated with Zelan AP[4] at a nominal 6.5% on the goods. Changes in dimensions were determined from changes in thread count. Related fabrics were finished together, in a single roll.

The treatment with a water repellent may seem incompatible with the desired swelling. It was employed because fabrics for garments would have been finished in this way to resist the entrance of water in order to postpone wetting and gain of weight; upon breakdown of the finish the cloth should continue to resist water by swelling.

Change in Fabric Texture

In order to help explain the decrease in water resistance upon finishing, experimental fabrics were sampled in the grey and after each step in finishing,

and then tested to show any changes in texture and closing capacity (Table IV). Fabrics labelled "scoured" in the tables and discussion were scoured only, "dyed" fabrics were scoured and then dyed, and "finished" fabrics were scoured, dyed, and finished with a water repellent. Results from tests of samples after scouring come nearest to representing the intrinsic capacities of fabrics for closing by swelling; results after dyeing show what could be expected if there were no final repellency treatment. Tensions during finishing had been kept at a minimum, as a precaution, but a study of several commercial fabrics at different steps in finishing showed that the ordinary tensions in a plant may not cause enough stretching to detract from water resistance.

There were three indications of what happened during finishing. 1. A small net shrinkage in fabric area, which implied a slight closing of texture. It appeared during scouring and persisted to the finished fabric. 2. An increase in air permeability upon scouring which showed that there had actually been a slight net opening, instead of closing, of texture. However, air permeability decreased a little upon dyeing and further upon Zelan treatment, thus indicating slight subsequent closing effects, possibly explainable by the addition of small amounts of material in these processes [1, p. 52]. 3. An increase in leakage of water through preswollen samples from step to step in finishing, which might indicate increases in openness, but was complicated by losses in swelling capacity.

The progressive increase in openness of texture might seem to be explained by an increase in compactness of yarn and accompanying slight increase in interspace in the cloth due to compression of the yarn by tension and pressure on the wet piece during finishing. However, such changes were judged from air-flow and orifice-test data [1, p. 51] to be not a controlling factor in change of texture.

Another mechanical effect, arising from the removal of noncellulosic constituents, is much more significant. Published analyses [7] giving amounts of such constituents indicate that 4–5% should be readily removed in the scouring of a mature-cotton

TABLE IV. Effects of Finishing Processes on Air and Water Resistance

Number	Maturity of cotton, %	Cloth construction	Air permeability, ft.³/min./ft.²	Hydrostatic pressure head, cm.	Hydrostatic leakage (86 cm. head), ml./5 min.		Seepage in orifice test, ml./10 min.
					Air-dry	Prewet	
101 G*	74	122 × 54	0.93	73	—	382	5.9
S		122 × 51	1.26	15	—	1033	13.2
D		123 × 51	1.08	19	—	1700	15.3
F		124 × 53	0.90	62	—	1900	15.9
102 G	74	122 × 60	0.48	82	—	67	—
S		122 × 59	0.78	23	—	170	—
F		124 × 60	0.57	78	—	476	—
114 G	85	124 × 56	0.87	65	177	1173	10.2
S		128 × 56	0.96	16	1974	1276	23.4
D		128 × 55	0.90	16	2241	1963	25.1
F		128 × 56	0.87	55	259	2186	26
118 G	85	124 × 72	0.09	95	9.5	20	13.6
S		129 × 72	0.24	23	201	44	—
D		130 × 69	0.39	35	298	173	—
F		130 × 70	0.15	74	8.5	126	32.7
119 G	30	124 × 56	0.21	88	4.8	29	0.53
S		129 × 56	1.89	7	1012	473	3.4
F		130 × 56	0.57	51	1609	1962	7.6
123 G	30	125 × 73	0.00	116	0.1	0.1	0.77
S		130 × 74	1.80	7	72	17	—
F		130 × 71	0.57	53	1456	176	11.4

* G = grey, S = scoured, D = dyed, and F = finished.

TABLE V. Swelling at Different Steps in Finishing (Centrifuge Method)

Maturity of cotton, %	Fabric number	Picks per inch	Swelling of yarns from fabrics, % volume			
			Grey	Scoured	Dyed	Finished
85	114	56				
85	118	72				
		Average	52.2	47.8	40.3	36.1
30	119	56				
30	123	72				
		Average	72.9	63.3	49.4	41.2
			Swelling of fabrics, % volume			
			Grey	Scoured	Dyed	Finished
85	114	56	43.8	42.4	35.7	31.4
85	118	72	36.4	35.3	32.0	29.1
30	119	56	58.0	56.9	46.5	38.0
30	123	72	48.6	47.7	42.2	34.8

fabric; and about 4% more, or roughly twice as much, from a very immature cotton of 45–50% lower maturity than the first [9, p. 30]. Such losses undoubtedly leave corresponding amounts of air space. This view was supported by calculation of the losses during finishing from observed changes in weights and areas of the fabrics made from cottons of 85% and 30% maturities. There was about 4.4% greater loss from the fabrics of immature cotton, a large factor in the greater leakage through preswollen immature-cotton fabrics.

Reduction of Swelling Capacity During Finishing

Since there is no practicable method for the direct measurement of the contribution made by the swelling of fibers to the closing of a fabric, additional evidence regarding the effects of swelling has been obtained from special tests using orifice, centrifuge, and hydrostatic methods.

Orifice tests showed that reduction of swelling capacity was a most important contributor to loss of water resistance upon finishing. Seepage through yarns taken from fabrics at the different steps in finishing (Table IV) invariably increased from step to step. This seems necessarily due largely to progressive decrease in swelling capacity because fineness of cotton and compactness of yarn remain practically unchanged.

More specifically, all yarns tested from scoured fabrics, whether made from mature or immature cotton, showed more seepage than yarns from the same fabrics before scouring. While it may be contrary to expectations, this indicated a lower degree of swelling in scoured than in grey yarn. Greater seepage through yarn from dyed cloth than through yarn from either grey or scoured goods indicated a further loss in swelling capacity; and the final still greater seepage through yarn from finished water-repellent fabrics indicated a still greater loss.

The amount of water retained upon centrifuging under suitable conditions has been rather generally accepted as a good indication of the relative amount of swelling of cellulosic fibers. Retention can be expressed as swelling by volume (Appendix) and selected values [1, p. 60, Table II] are given here in Table V. The average values for swelling of yarns taken from two fabrics made from the same lot of mature cotton decreased considerably from step to step in finishing. The corresponding samples from the immature-cotton fabrics swelled more than those from the mature, but their swelling capacity decreased at a greater rate during finishing. An initial 20% greater swelling of yarn from the grey immature-cotton fabric over that from the mature was reduced to only 5% in the finished materials; and this 5% was probably offset in large part by about 4% greater loss of noncellulosic constituents of the immature cotton from scouring.

Fabrics swelled less than yarns (Table V) and the more tightly woven fabrics swelled the least. The finished immature-cotton fabrics swelled about 6% more than the mature. Although greater swelling of immature cotton was shown, its effect in

closing the fabric would probably be largely offset by the loss of its larger proportion of noncellulosic constituents.

The values obtained for the swelling of the grey yarns, 52.2% and 72.9% for mature and immature cottons, respectively, are higher than the values reported for the swelling of cotton as estimated in some other ways. The high values have not been fully explained but are comparable with examples of other high values quoted in one of the original publications [1, p. 53].

The chance that the yarns and fabrics of fine, immature cotton held more water in their capillary systems in the centrifuge tests and that it might be mistaken for water of swelling is ruled out by the method of extrapolation used [8].

Some of the hydrostatic tests on fabrics also afforded evidence of the reduction of swelling capacity by finishing. Leakage usually increased progressively through samples taken at the different steps in finishing, when preswollen and tested under a fixed hydrostatic head. The changes were large enough to indicate a considerable decrease in swelling capacity (Table IV, and [10, p. 48, Table V]).

Finishing without Scouring

On account of the great loss of closing capacity upon scouring, this step was omitted in the finishing of a few samples, even though a boil or scour has been considered essential for satisfactory dyeing. Fabrics were simply wet-out in water containing a wetting agent, dyed, and treated with Zelan for comparison with goods finished as usual [10, p. 49, Table VIII]. Of the dyed fabrics not Zelan-treated, those not scoured were less permeable to air than the scoured (and dyed) fabrics, and less permeable to water after preswelling. After Zelan-treatment, all fabrics not scoured were less permeable to air, in some cases much less; and they were much less permeable to water when tested preswollen. The opening-up of fabrics by scouring was thus demonstrated by direct tests. If the materials removed could be left in the goods, there would be a distinct gain in capacity to close by swelling.

Special Effects of Mercerizing

Mercerization of cloth for water-resistant goods of medium weight is apparently intended mainly for better absorption of dye and repellency agent and for dimensional stability. Mercerization under tension is known to increase the openness of texture of many fabrics. However, it seems to be widely thought that mercerization of cloth without tension will shrink and thereby close it. This is not necessarily true. Examples given earlier [10, p. 44 and Table VI] include a fabric shrunk in mercerizing which was nevertheless opened somewhat, according to permeability tests, in comparison with the original unmercerized material, in spite of an 18% reduction in area. A contrast was afforded by a fabric of much higher pickage, shrunk about 3% in mercerizing and finished as usual; in comparisons preswollen, it leaked more than in the grey unmercerized, but less than when finished unmercerized. From such evidence it has been concluded that piece mercerization of very high pickage goods may contribute to ability to close by swelling and to a highly water-resistant product.

Significance of Swelling

Test results in the past may have led to the impression that swelling contributed more to water resistance than was actually the case. The significance of swelling cannot be judged, for example, by the hydrostatic head required to start leakage of water. To illustrate possible inconsistencies, in a group of five related grey fabrics, the one that required the highest head in the usual test of air dry fabric leaked the most when tested preswollen for amount of leakage. This fabric seemed most resistant in one test but least resistant in the other. Conversely, the sample that seemed least water-resistant, because it required the lowest head, leaked the least preswollen so that it seemed best in this test. After the fabrics of this group were finished, one leaked three times as much as another even though they required equal heads in the usual hydrostatic test. Obviously there is not necessarily any connection between hydrostatic head and effectiveness of swelling.

In other experiments, two fabrics made from mature cotton were tested for amount of leakage both air dry and preswollen, in the scoured and in the finished states, at a fixed head of 86 cm. of water. There was less leakage through the finished fabrics air dry than preswollen (Nos. 114 and 118, Table IV) but this should not be mistaken for a greater closing effect by swelling. However, samples of the same fabrics scoured only, which must have swollen more easily than the finished samples, were not nearly as well closed as the latter in the test air dry.

TABLE VI. Densities, Swelling, and Closing of Fabrics

Fabric number	Maturity of cotton, %	Cloth construction	Bulk* density, g./cm.³	Distribution of† fabric volume		Swelling and volume† relations in fabrics			Hydrostatic leakage, Suter (pre-swollen), ml./5 min.
				% Cotton	% Air space	% Swelling necessary to fill volume	Observed swelling, %	% Volume filled	
101	74	122 × 54	0.69	40	60	150	—	—	382
118	85	124 × 72	0.80	46.4	53.6	115	36.4	63.3	20
118 F‡	85	130 × 70	0.83	48.2	51.8	107	29.1	62.2	126
123	30	125 × 73	0.79	45.8	54.2	118	48.6	68.1	0.1
123 F	30	130 × 71	0.83	48.2	51.8	107	34.8	65.0	176
105	74	122 × 71	0.83	48.2	51.8	107	—	—	0.0
105 F	74	122 × 71	0.87	50.5	49.5	98	—	—	9.2

* Bulk densities were calculated from thickness and weight per sq. yd (air dry).
† Calculated according to original paper [1, page 58; see also Table II, p. 61].
‡ "F" indicates finished.

Such results show that the water resistance, even of a very tightly woven finished fabric (No. 118), may not be affected to any important degree by swelling.

Fabric Density and Closure by Swelling

A study of bulk densities of some of the experimental fabrics as related to closing by swelling lends further support to the conclusion that swelling can actually close a fabric only under most favorable conditions of construction. If the tightness of a fabric is increased by the addition of more picks per inch, the density in its central zone will be increased. Since this density could not be determined because of a density gradient from surface to center, bulk densities of air dry experimental fabrics were estimated in grams per cubic centimeter from thicknesses and weights per square yard (Table VI). That only very tight, dense fabrics can possibly close by swelling will become evident from the consideration of bulk densities and the relationships between swollen cotton and air space within the fabrics [see also 1, p. 61, Table IV]. In the examples to be given, it is assumed that the fabrics did not change in over-all volumes upon wetting and swelling.

The bulk density of the first fabric (Table VI) was 0.69 air dry. When allowance was made for 7% regain, the calculated [1, p. 58] volume of cotton, the basis for estimation of swelling, was 40% of the volume of the fabric. The rest of the volume was air space, 60%, and in order to fill this space completely by swelling, the cotton would have had to swell by 150%. As would be expected, this fabric did not close by swelling.

Two fabrics, Nos. 118 and 123 were considered to have closed by swelling when in the grey (unfinished) state, although not after finishing. The grey fabric of bulk density 0.8 had 46.4% of its volume occupied by cotton and 53.6% by air space. Here the cotton would be required to swell by 115% to fill all the space; but this is more than cotton can swell in water. Moreover, the actual swelling capacity of this cotton in its fabric form was estimated (Appendix) by a centrifuge method to be only 36.4%. Hence, if the 46.4% of cotton in the fabric swelled by 36.4%, it would bring the swollen volume of cotton up to only 63.3% of the total fabric volume. Although this fabric came 37% short of being filled, it was practically closed to the passage of water. The other fabric (No. 123) was about 32% short of being completely filled by the swollen cotton. Undoubtedly, these fabrics closed because of swelling in their zones of maximum density. Their failure to close after finishing, emphasizes again the narrow range in which swelling has much significance.

Fabric No. 105, highest in bulk density of all the experimental fabrics, came so near to closing after finishing that it was considered to be of swelling type when finished as well as in the grey, where it was definitely of swelling type.

Entrapped Air as a Factor in Water Resistance

It is recognized that in ordinary water repellency, air held within a fabric may help to resist the

passage of water. However, under conditions to be described, entrapped air may have much more than its usual effect. This is illustrated (Table VII) by two fabrics of high pickage, finished as usual with Zelan. After a sample of each fabric was exposed to the prevailing laboratory atmosphere (Experiments No. 1 and 7) and similar samples (Nos. 2 and 8) were exposed over water in a presumably saturated atmosphere, the second samples required higher heads for the penetration of the usual 3 drops of water in a Suter hydrostatic test. When other samples, similarly exposed to air and to water vapor, were tested for amount of leakage at a constant head of 86 cm. of water, the ones exposed to water vapor leaked much less than those exposed to air.

Such results might be attributed to swelling of the fabric by the water vapor. However, after the selfsame exposed samples were boiled in water to drive out air and to swell them, they leaked far more under the same head than in the previous tests. These last leakages corresponded roughly with those observed in the same test when samples of fabric were fully preswollen (Nos. 3, 6, and 10).

Since the amounts of water taken up (regain) by the preswollen samples were two or three times as great as the amounts taken up by the vapor-exposed samples, it seems clear that the extra 9–10% in the latter, above the 5–6% in the ordinary air dry samples, did not cause very great swelling. Hence the superior water resistance of the vapor-exposed samples is attributed to air within the fabric which must be held in some more effective way than usual.

In another case, a sample of one of these same fabrics was held under water at room temperature for 1 hr. under a head of 100 cm., and another for 24 hr. When these were blotted free from excess water and tested for amount of leakage under the 86 cm. head, the first (No. 4 in Table VII) leaked only 1 ml., but the second (No. 3) 115 ml. Seemingly, the first of these two samples (No. 4) leaked less than the air dry sample (No. 1) because of greater swelling. However, the sample held under water for 1 hr., which then had only 19% regain moisture, could not have swollen as much as the one kept under water for 24 hr., with its regain of 46%. Yet, the latter, which should apparently have swollen most, leaked far more than either the air dry or the 1-hr. sample.

It is difficult to see how water repellency could, of itself, make samples of fabric containing 15% to 19% regain moisture more water-resistant than samples of the same fabrics with only 5% to 6% regain. The alternative seems to be air held in some particular way within the fabric structure; and a

TABLE VII. Effects of Methods of Preswelling on Leakage Through Fabrics

Fabric number	Experiment number	Treatment	Moisture regain,* %	Hydrostatic head, cm.	Leakage, Suter (86 cm. head‡), ml./10 min.	
					Original**	After 3 min. boil
117 F (128 × 66)	1	Control, air dry	5.8	73	17	292
	2	22 hr. in water vapor	14.8	87	0.4	163
	3	24 hr. (80° F.) 100 cm. head	46.1†	—	115	240
	4	1 hr. (80° F.) 100 cm. head	19.3†	—	1.0	452
	6	1 hr. boil, 50 min. soak (80° F.)	51.1†	—	401	344
131 F (128 × 64)	7	Control, air dry	5.5	69	63	681
	8	22 hr. in water vapor	15.2	79	13	625
	10	10 min. boil, 24 hr. soak (80° F.)	37.5†	—	425	—

* Based on dry weight of cotton.
† Determined after light blotting of samples.
‡ Note that leakages were observed for 10 min. intervals rather than 5 min. as in other tables.
** As described in the third column.

similar explanation seems to apply to the sample immersed for 1 hr. It retained some of its enclosed air, which was free to become saturated with vapor from the surrounding water, and to remain in this state while immersed. Hence, the cotton had been exposed to water vapor very much as in the direct exposure, and air and moisture might have been held in the same way to make the fabric more water-resistant.

It could be inferred that tightly constructed, water-repellent fabrics could become more water-resistant if they should happen to be worn in very humid or foggy weather immediately before being exposed to rain. In fact, the absorption of water vapor with gain in water resistance might even take place under ordinary conditions within the cloth in a garment worn in the rain.

Conclusions

Fabrics which closed against the passage of water under test conditions by the swelling of their constituent fibers were made from carded yarns of ordinary American cottons. Experimental fabrics which did close by swelling in the grey or loom state, tended to lose that capacity upon finishing. They would be difficult to manufacture, even as grey goods, and conventionally finished goods of strictly swelling type would apparently be especially difficult to produce. Fabrics of the required density or tightness would be undesirable in clothing, unless for some rather special purpose.

To achieve the highest possible closing by swelling, methods might be required which would be impractical and too expensive for ordinary large scale manufacture. One such method would be to scour the yarns, mercerize them under tension, perhaps dye them, and then weave them without warp sizing into the tightest possible fabrics of very high pickage. Alternatively, scoured yarns might be woven very tightly and the fabrics mercerized in the piece without tension. In either case, the cloth could be treated in the piece with a water repellent if that were needed.

Air entrapped within a tightly woven, water-resistant fabric may be as effective in preventing leakage of water through it as would be closure of the very last of the interspace by swelling. If this entrapped air could be proved to be effective in service, the weaving of the very tightest possible fabrics and the achieving of complete stoppage by swelling might not be necessary.

Extremely immature cotton, in spite of its limitations, may be of interest for making cotton fabrics of moderate weight and high impermeability to air or dust, as well as to water, if the fabric does not have to be scoured. The fairly large amounts of very immature cotton reported to be frequently available, and for which there has been a limited market, might help make such a development possible.

Appendix: Methods of Testing Yarns and Fabrics

Physical properties of yarns and fabrics were determined by current A.S.T.M. methods.

Tests for water resistance included conventional tests to show the quality of the fabrics in familiar terms and special tests to bring out the part played by swelling. The choice of conventional tests has been explained [2, p. 17]; a few changes were made in procedure on account of the exceptionally high water resistance of some of the fabrics. The less familiar Bundesmann apparatus normally provides a shower at the rate of 3 in. of water in 10 min. Its use and results have been explained [2, p. 16].

The relative degree of closing of a fabric as an effect of swelling was determined on test pieces preswollen by boiling in distilled water for 10 min. and then being allowed to stand in cold water to a total of 1 hr. [2, p. 15]. In most tests, the column of water in a Suter hydrostatic apparatus was set at a constant head of 86 cm. above the preswollen test piece and the amount of water that passed through it in the given time interval was measured.

The centrifuge was used in the manner described by Welo and his associates [12] and Preston [8] for the estimation of the weight of the water of swelling [1]. This water, as regain retained by the dry cotton, is considered to be additive as volume to the volume of cotton that corresponds with its density in water, 1.61 [5, p. 95]. The corresponding specific volume is 0.621 $cm.^3$, so percentage of regain divided by 0.621 gives the percentage of volume added by swelling [1, p. 58].

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Treatment of Wool with Chlorosulfonated Polyethylene

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Introduction

Modification of the properties of wool by treatment with polymeric materials has been known for many years. The polymer may be preformed and applied to the wool or formed in or on the fiber, as desired [2, 7]. Regardless of the technique of application, it is usually desirable for the polymer to have groups capable of reacting with the functional groups of the wool to anchor (i.e., graft) the polymer permanently to the wool fiber. Chlorosulfonated polyethylene is such a polymer, containing $—SO_2Cl$ groups which are generally capable of reacting with $—NH_2$ and —OH groups. The physical properties of the polymer film exhibit many of the desirable features needed in a resin finish. It is resistant to sunlight, weather, ozone, abrasion, flexing, flame, water, and a wide variety of chemicals and solvents [9, 8].

The use of chlorosulfonated polymers in conjunction with fixative agents to cross-link the resin deposited on the wool is reported in the patent literature [4]. However, the application of chlorosulfonated polyethylene without cross-linking agents has apparently not been investigated. Accordingly this investigation was undertaken to determine whether the polymer could be anchored to the wool without the use of fixative agents and to examine some of the chemical and physical properties of the modified wool.

Materials and Procedures

Description of the Resin

Hypalon 20.[2] The polyethylene used for chlorosulfonation has a number average molecular weight of 20,000. The chlorosulfonated material contains on the average one chlorine atom every six or seven atoms along the backbone chain and one sulfonyl chloride group for about every 100 carbon atoms (i.e., 8 per polymer molecule) [9, 8]. Sulfonyl

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[2] Mention of specific products does not imply recommendation by the Department of Agriculture over others of a similar nature not mentioned.

chloride groups are generally capable of reacting with $—NH_2$ and —OH groups. If this occurs in the resin-treated wool, it should chemically anchor the polymer to the wool fiber.

Wool Fabric

A 6.12 oz./sq. yd. worsted wool flannel fabric containing 64 ends and 55 picks/in. was used. The flannel was extracted in a Soxhlet extractor with ether for 8 hr., followed by ethanol for 8 hr., then dried 12 hr. at 45° C., and conditioned at 70° F. and 65% RH (standard conditions). Swatches, about 6 × 5 in. (W × F), conditioned and weighed before and after treatment, were used.

Application of Resin and Evaluation of Treated Fabrics

By reaction from solution. In principle, this is an exhaustion procedure. Wool flannel swatches were immersed in toluene or decalin solutions of the polyethylene resin in a flask equipped with reflux condenser, thermometer, and heating mantle, and heated for 3–6 hr. at 55° to 110° C. in an attempt to induce reaction of the $—SO_2Cl$ groups of the resin with $—NH_2$ or —OH groups of wool to yield surface graft polymers.

Pad, dry, and cure procedure. This is the preferred procedure for applying these resins to the wool fabric. The sample is wet out in a toluene solution containing 2–12% resin and passed through the squeeze rolls of a small laboratory padder to remove excess solution, air dried and then heated in a laboratory oven of known temperature for the specified time. The cured swatches are equilibrated under "constant temperature and humidity" conditions to estimate the uptake of resin.

Solvent extraction of treated swatches. To determine how much of the incorporated resin was permanently anchored to wool, resin-treated swatches were immersed in toluene and refluxed for 2–4 hr., the solvent decanted, fresh solvent added, and the process repeated twice. The samples were then rinsed several times in fresh solvent, dried, and equilibrated under standard conditions. The amount of resin extracted was determined by weight difference.

Flexural rigidity. The cantilever procedure, ASTM D 1388-55T, was used to determine flexural rigidity of the resin-treated wool flannel swatches.

Tear test. The Elmendorf falling pendulum tester was used according to the directions of ASTM test method D 1424-56T [3].

Shrinkage tests. The Accelerotor [10] was used to test the shrinkage resistance of the resin-treated flannel swatches. The conditions were 1780 r.p.m., 2 min., 200 ml. 0.5% Na oleate, 40° C., preconditioned in 1% NaOAc, 10-cm. marks, 6 × 5 in. swatch.

Tensile strength. Dry strength and elongation measurements were made using the cut-strip method, ASTM D 39–49.

Abrasion resistance. An Accelerotor abrasion method was employed [5]. Flannel swatches 4 in. sq. were used; edges were sealed with Ubabond cement. These were abraded for 2 min. at 3000 r.p.m. in the Accelerotor using 180 grit. The extent of abrasion was determined by weight loss, the samples being conditioned to standard conditions before all weighings. The percent abrasion was taken as the average on ten samples for the control and for each resin loading.

Wrinkle recovery. ASTM test method D 1295-53T was employed, using the Monsanto Wrinkle Recovery Tester.

Acid solubility. The method of Zahn and Würz [11] was employed. Decrease in weight following exposure of the sample to 4 *M* HCl at 65° C. for 1 hr. was used as a measure of the solubility.

Peracetic acid solubility. Weighed samples of wool were immersed in 100 ml. of 2% peracetic acid for 25 hr. and treated subsequently for 24 hr. with 150 ml. of 0.3% ammonia [1]. The loss in weight was used as a measure of solubility in this solvent.

Alkali solubility. The method of Harris and Smith [6] was used to determine the solubility in alkali. Weighed samples of wool were placed in 0.1 *M* NaOH at 65° C. for 1 hr., and the loss of weight was used as a measure of the solubility.

Dry soiling. This is a qualitative test to compare the soiling tendency of treated and untreated wool fabrics. The soiling mixture consists of 10 parts by weight Norite C carbon black and 90 parts by weight anhydrous sodium sulfate. A test swatch and a control swatch (each about 4 in. sq.) are placed in a jar (8 cm. diameter by 20 cm. height) with 1/10 their weight of soiling mixture and ½ lb. of lead shot and shaken vigorously by hand for 1 min. This is followed by vacuum cleaning of the swatches and visual comparison of their relative soiling tendency.

TABLE I. Reaction of Chlorosulfonated Polyethylene Solution with Wool Flannel *

Sample	Solvent	% Resin in solvent	Pretreatment	Time, hr.	Temp., ° C.	% Resin uptake	% Area shinkage
1	Decalin	10	None	3	55	1	Not measured
2	Decalin	10	Dried 1 hr. 105° C.	3	55	1	Not measured
3	Decalin	10	None	3	55	1	41.5
4	Toluene	10	Dried 1 hr. 105° C.	6	110	1.8	54.5
5	Toluene	10	Bleached with peroxide (not extracted)	6	110	0.4	43.8
6	Toluene	10	Scoured with detergent (not solvent extracted)	6	110	0.4	43.0
Control		None	—	–	—	—	45.0

* Exhaustion procedure.

TABLE II. Shrinkage Versus Resin Uptake for Treated Fabric *

Sample (cured 2 hr., 110° C.)	% Resin on fabric	% Area† shrinkage	Flexural rigidity‡ after accelerotor wash, mg. cm.
1	15.7	0.0	Not measured
2	14.2	3.0	189
3	8.5	3.0	159
4	5.3	14.5	150
5	3.5	37.0	Not measured
Control	0	46.0	143

* Treated by padding procedure.
† Determined by 2 min. wash in Accelerotor.
‡ Cantilever procedure, ASTM Method D 1388-55T

Results and Discussion

The sulfonyl chloride groups of chlorosulfonated polyethylene proved to be less reactive with the $—NH_2$ and —OH groups of wool than had been anticipated. In the exhaustion technique very low uptakes of resin were realized even under a wide variety of conditions (See Table I). Of course, the polymer molecule is too large to diffuse to the interior of the fiber and reaction is consequently limited to the fiber surface. When the surface $—NH_2$ and —OH groups have reacted, there remains no further mechanism by which additional polymer can react with the wool. In effect it appears that a unimolecular film of grafted polymer is obtained by the exhaustion procedure. That this is the case is suggested by experiments in which greater amounts of polymer were deposited by the padding procedure and cured at 110° C. In these instances the amount of polymer remaining after toluene extraction is about the same as the quantity deposited from solution by the exhaustion procedure.

The data of Table II show it is not necessary to have the resin anchored to the wool, nor to have the resin film itself cross-linked by addition of cross-linking agent to the polymer during application to wool, in order to impart good shrinkage protection to the wool. That little or no cross-linking occurred in the polymer film itself during curing or between wool and the polymer molecules at lower temperatures of cure is shown by the extractability of more than 80–90% of the resin with toluene (Table V).

The durability of the resin finish to laundering is good even though the resin is not grafted to the wool or cross-linked with itself (Table IV). It would, however, have less durability to dry cleaning solvents. When the resin is extracted with toluene, the fabric is no longer resistant to shrinkage, as shown by the data of Tables II, V, and VI. In all cases, regardless of the initial resin uptake, the samples lost their shrinkage protection when the resin was solvent-extracted. This was as expected, perhaps, except for the possibility that small amounts of grafted resin would be sufficient to impart shrinkage protection. The resin not extracted by solvent is presumed to be grafted to the wool fiber.

It is possible to increase the amount of resin grafted to the wool by going to longer curing times

TABLE III. Mechanical Properties of Resin-Treated Flannel

Sample (cured 2 hr., 110° C.)	% Resin on fabric	Break strength, lb./in.²	Flexural rigidity, mg. cm. (no mechanical conditioning)*
1	12.3	29.1	368
2	9.6	36.6	322
3	5.3	33.7	255
4	3.5	34.1	251
Control	0	30.1	143

* Cantilever procedure.

TABLE IV. Durability of Resin Finish to Laundering

Sample (cured 2 hr., 110° C.)	% Resin	% Area shrinkage: Accelerotor wash #* 1	2	3	4	5	6	7
1	15.7	0	1.0	4.9	7.8	—	—	
2	9.7	1.0	2.0	4.9	7.8	9.8	15.4	
3	8.7	1.0	3.0	3.0	3.0	4.9	14.5†	
Control	None	46.0	—	—	—	—	—	

* 2-min. washes; 1780 r.p.m., 0.5% Na oleate, 40° C., 10-cm. marks.
† 10-min. wash in Accelerotor.

TABLE V. Extractability of Resin with Toluene

Sample (cured 2 hr., 110° C.)	% Resin on fabric before extraction	% Resin on fabric after extraction	% Area shrinkage* extracted sample
1	12.9	0.7	43.8
2	7.8	0.8	46.0
3	5.0	0.8	46.7
4	3.6	1.2	46.8
Control	None	—	45

* Accelerotor shrinkage test.

TABLE VI. Extent of Resin-Grafting as Function of Curing *

Sample	Curing conditions: Temp., ° C.	Time, hr.	% Resin on fabric: Before extraction	After extraction†	% Area Shrinkage after extraction‡
1	128	2	9.0	1.9	42.4
2	128	4	9.2	1.9	40.9
3	128	6	9.2	1.8	40.0
4	128	22	8.3	4.7	0.0
5	105	3	9.8	1.9	—
6	105	5	9.4	1.5	45.3
7	105	7	9.4	1.7	43.1
8	105	23	9.4	1.6	43.1
9	130	24	7.6	4.3	1.0
10	130	24	5.4	4.0	1.0
11	130	24	3.3	2.4	1.0
12	130	24	0.8	0.5	12.6
13	150	18	7.8	7.0	0
14	150	18	4.3	3.4	1.0
15	150	18	1.6	0.8	0
16	150	18	1.7	1.1	1.0
Control	150	18	—	—	51.0

* The padding procedure of application of resin was employed in these tests. % Resin on fabric is varied by changing concentration of padding solution.
† As determined by toluene extraction.
‡ As determined by Accelerotor shrinkage.

and higher temperatures, as shown by the data of Table VI covering a greater variation in the conditions of the padding and cure technique. At 128° C., only 20% of the total resin present is grafted after 6 hr. compared with 57% grafting after 22 hr. At 105° C., only 17% of the resin is grafted after 23 hr. At 130° C. and 24 hr., the extent of grafting varies somewhat, depending on the quantity of resin initially present (Experiments 9–12, Table VI). At 150° C., up to 90% of the resin is grafted after 18 hr. (Experiments 13–16, Table VI), and good shrinkage protection is observed for all samples, two of which contained only 1% resin. That this shrinkage protection was not due to the curing conditions per se is shown by a control which shrank 51%, about the same as regular, untreated flannel. At 150° C., however, the wool is badly yellowed.

These experiments demonstrate that it is possible to form graft polymers between chlorosulfonated polyethylene resins and wool under sufficiently drastic conditions (130–150° C. and 18–24 hr.). Under milder conditions, grafting occurs only to a small extent. Grafting of the polymer to the wool is not necessary to impart good shrinkage protection, and resistance to acids, alkali, and oxidizing aqueous solutions, and to give reasonably good durability to the resin finish on the wool. However, grafting should result in improved resistance to removal by dry cleaning solvents and would possibly give better shrinkage protection and durability of resin finish at lower resin uptakes than does ungrafted material.

The treated fabric possesses many desirable features in addition to those of untreated flannel. The good resistance to shrinkage during laundering has been mentioned previously. The durability of the finish to laundering appears to be quite good also. The handle of the treated fabric is a bit harsher than that of untreated material before washing, particularly at higher resin loadings; this is revealed by the flexural rigidity measurements shown in Table III. However, after washing, the flexural rigidity is greatly improved and the handle is quite good, as shown in Table II.

TABLE VII. Abrasion Resistance of Resin-Treated Fabric *†

Sample	% Resin	% Abrasion	Break strength after abrasion, lb./in.²
1	7.4	4.4	29.2
2	3.3	4.1	30.6
3	None	2.8	30.1

* Accelerotor abrasion method. Samples abraded 2 min. at 3000 r.p.m. using 180 grit.
† Resin cured 2 hr., 110° C.

TABLE VIII. Wrinkle Recovery of Resin-Treated Wool Flannel *†

Sample	% Resin	Wrinkle recovery, deg.‡ Warp	Fill
1	1.8	153	151
2	3.6	154	156
3	7.2	154	155
4	14.3	151	152
5	None	146	146

* Wrinkle recovery determined by ASTM Method D 1295–53T using Monsanto Wrinkle Recovery Tester.
† Samples cured 2 hr., 110° C.
‡ Samples not mechanically conditioned following resin application.

The color of the treated fabric is very good, being not detectably different (to the eye) from untreated flannel. Exposure of samples containing from zero to 12% resin to the ultraviolet light from a germicidal lamp for seven days gave about the same extent of yellowing, independent of the amount of resin.

The treated samples develop no odor even after extended washings. Soiling tests on the treated fabrics were made with carbon black. Treated fabric does pick up somewhat more carbon than the untreated.

Some of the mechanical properties of the fabric are shown in Tables III, VII, and VIII. The break strength, wrinkle recovery, and abrasion resistance are not significantly different from those of untreated flannel.

An outstanding advantage obtained by the resin treatment is the greatly improved resistance to attack by alkali, acids, and oxidizing media. The results shown in Table IX demonstrate the improved resistance to these media as a function of the amount of resin on the fabric. For periods shorter than 24 hr. (the period used in the peracetic acid solubility test) significantly greater resistance to peracetic acid was evident. Also, significant resistance to hypochlorite bleach was observed. Strips of the treated fabric placed in 6% hypochlorite bleach took up to 24 hr. to dissolve completely, compared with 15–20 min. required to dissolve untreated flannel.

TABLE IX. Solubility of Resin-Treated Wool Flannel

Sample cured 110° C., 2 hr.	% Resin on wool	% Solubility Acid*	Alkali†	Peracetic acid‡
1	12.3	7.1	4.5	72.1
2	9.6	10.9	8.6	79.5
3	5.3	13.0	9.6	81.2
4	3.5	15.4	11.3	84.1
Control	None	17.6	11.4	86.4

* 4 *M* HCl, 65° C., 1 hr.
† 0.1 *M* NaOH, 65° C., 1 hr.
‡ 2% peracetic acid, 24 hr., 25° C.; treated subsequently with 0.3% ammonia, 24 hr.

Conclusion

It is possible to graft polymers of chlorosulfonated polyethylene on wool by curing at 130–150° C. for 6–24 hr. Under milder conditions of cure only 1–2% resin is grafted. Although deposition of the resin on wool without grafting, at uptakes of 8% or higher, gives treated fabric with good resistance to shrinkage, durability of the resin finish to laundering, and good resistance to aqueous solvents, grafting is necessary to give durability of the treatment to dry cleaning. Also, the grafting of the polymer affords the desired properties at lower resin uptakes. The treated fabric is not significantly altered in hand, wrinkle recovery, abrasion, tear strength, or color; it does show a somewhat greater tendency to soil, as revealed in tests using carbon black.

Acknowledgments

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Introduction of Vinyl Groups into Wool Fiber

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Introduction

The primary objective of this study was to develop synthetic procedures for introducing vinyl groups into wool fiber. This paper presents the techniques employed for vinylation and attempts to characterize the reaction involved.

Vinylated wool is of particular interest as an intermediate in graft polymer formation. The presence of vinyl groups in wool might also have beneficial effects per se, such as increased stability to light and heat [4] or increased resistance to oxidative degradation.

Research related to these various interests will be presented in future publications.

Experiments and Results

Source and Preparation of Materials

The wool flannel fabric was a 6.9-oz./sq. yd., 2/1 twill construction with 64 ends and 53 picks/in. Swatches 5 × 6 inches, weighing about 4.5 g. each were used. These were thoroughly extracted consecutively with ether and ethanol and then stored at constant temperature and humidity (21° C. and 65% RH) until used. The conditioned swatches were weighed, and the factor 0.883 was employed for correction to dry weight. Since the treatment of fabric prior to each vinylation reaction differed, the treatment will be described with each procedure.

The vinylating agents [2] used were acrylyl chloride, b.p. 74–76° C., ethyl acrylate, b.p. 99–100° C. (Borden), maleic anhydride ("white label") (Eastman), N,N′-methylenebisacrylamide (American Cyanamid), glycidyl methacrylate (du Pont), and N-carbamyl maleimide (Naugatuck).

Methods for Determination of Reactions

Direct chemical analysis for vinyl groups by conventional procedures is difficult because of the high reactivity of the wool with the reagents employed. For example, attempts to determine vinyl groups by addition of bromine from a standard bromide-bromate solution, by addition of iodine monochloride (Wijs solution), or addition of mercaptan across the double bond were unsuccessful.

Determination of vinyl groups by infrared and high resolution nuclear magnetic resonance is also difficult. The infrared spectrum of wool in potassium bromide pellets is poorly resolved, particularly in the region expected for vinyl group absorption. The NMR spectra of treated and untreated wool in sodium deuteroxide-deuterium oxide solvent gave evidence of modification with a peak present in the treated wool which is not present in the untreated. The assignment of the new peak has not been achieved.

Direct evidence for reaction is the increase in weight of the treated, thoroughly extracted wool and

[1] A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] Mention of specific products does not imply recommendation by the Department of Agriculture over others of a similar nature not mentioned.

TABLE I. Selected Examples of Vinylation Experiments

Sample no.	Treatment	Increase in weight, %	Amino N, %	Amino groups vinylated, %*	Hydroxyl groups vinylated, %
1	Untreated	0	0.31	0	0
2	Ethyl acrylate†	5.4	0.25	18.4	46.9
3	Acrylyl chloride‡	7.7	0.21	30.0	65.1
4	Maleic anhydride**	7.3	0.05	80.8	5.7

* Based on amino acid composition of wool in m. moles/g. wool [1] corrected for increase in weight.
† Wool swollen with dimethylformamide, then reacted with refluxing ethyl acrylate with sulfuric acid catalyst for 24 hr.
‡ Acetic acid solvent, 60° C., 3 hr., with dimethyl aniline to take up HCl.
** Acetic acid solvent, 58° C., 2 hr.

the accompanying decrease in Van Slyke amino nitrogen (Table I). The decrease in Van Slyke amino nitrogen may be attributed to reaction of the vinylating agent with a portion of the amino groups. By subtracting the percent increase in weight attributed to reaction with amine groups from the total percent increase, the percent reaction with hydroxyl groups can be obtained.

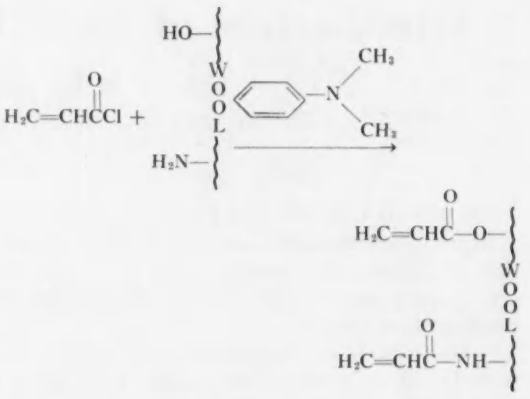
Evidence for the vinylation is obtained by determining to what extent possible competing reactions occur. One such reaction is the Michael type addition of amine or hydroxyl group across the double bond of the vinylating reagent, resulting in elimination of its vinyl character. Another possible competing reaction is the polymerization of the vinyl monomer inside the fiber to yield a non-extractable polymer which may or may not be chemically bound as a graft polymer.

To check the extent of these competing reactions, solutions of model compounds (amino acids such as glycine, lysine, alanine, serine, and cystine) and acrylic monomers (acrylamide and ethyl acrylate) were held under reaction conditions used in the vinylation experiments. The solutions were analyzed periodically by a bromide-bromate titration for change in acrylic monomer (double bond) concentration. The Michael type addition or polymerization would result in a decrease in vinyl group concentration. Little or no decrease was noted in these tests, demonstrating under the conditions used that vinylation was the predominant reaction.

A further check of the possibility of a Michael type addition consisted in reacting wool swatches with ethyl acrylate and acrylyl chloride (vinyl groups of about the same reactivity) in glacial acetic acid. If the reaction taking place were the Michael type the gain in weight would be approximately the same for each reactant, whereas, if it were of the vinylation type (nucleophilic displacement on the carbonyl group of the reagent) the acrylyl chloride would show greater reactivity. The ethyl acrylate-treated wool showed little or no increase in weight; the acrylyl chloride-treated fabric showed a gain in weight of 6–8% demonstrating again a marked preference for the vinylation reaction.

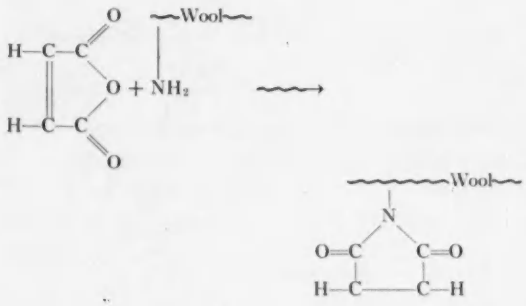
Reactions Studied

Acrylyl Chloride Treatment. It is postulated that reaction occurs with wool as follows:



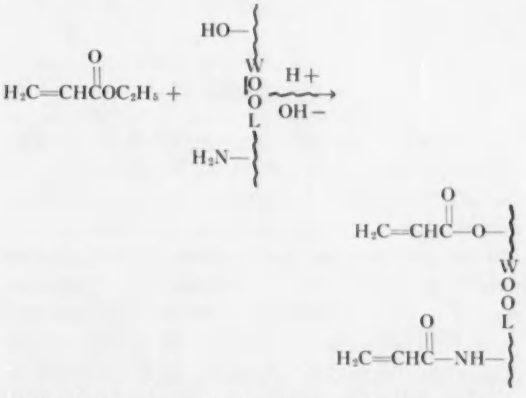
Wool swatches weighed under standard conditions were dried for 2 hr. at 105° C. and placed directly into the reaction flask. In one case the treatment solution consisted of 150 ml. of glacial acetic acid, 5 ml. of acrylyl chloride and 2 ml. of dimethylaniline. The swatch was heated at 60° C. for 3 hr., then washed with acetone 5 or 6 times and rinsed for 16 hr. under a stream of distilled water. After air drying for a few hours and drying at 105° C. for 2 hr., the swatch was weighed. A 7.7% gain in weight over the initial dry weight was observed. A similar experiment using dimethylformamide as solvent, and heating for 20 hr., gave a gain of 8.3%; in carbon tetrachloride, the wool showed less than 1.0% increase in weight upon refluxing (78° C.) for 3 hr. Variation in amount of reaction with change in solvent is presumed to be due to differences in the swelling power of the solvent for the wool fiber.

Maleic Anhydride. It has been suggested [2] that maleic anhydride reacts with wool in the following manner:



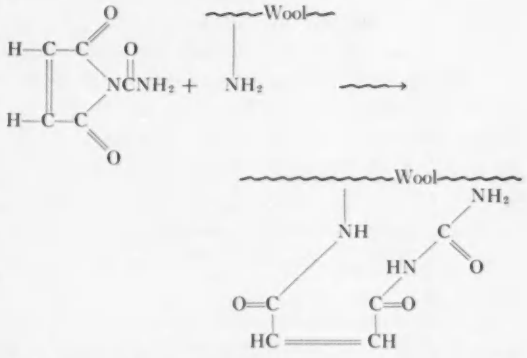
Several conditions and treatments were compared in the present study. The following procedures gave the best results. Each dried, weighed swatch was placed in a solution of 5 g. maleic anhydride in 200 ml. of carbon tetrachloride and heated to reflux for 2 hr. The swatch was thoroughly rinsed, first with acetone, then with water, and then dried at 105° C. for 2 hr. An increase in weight of about 1.5% over the calculated dry weight was obtained. When a reaction was conducted in the same manner with a fabric completely wetted out with distilled water (to a wet pick-up of about 100%), the increase in weight was about 9.4%. When a wool swatch was heated to 95° C. for 2 hr. in a solution of 200 ml. of dimethylformamide and 7 g. of maleic anhydride, the weight increase was about 19%. The procedure that consistently gave good results, with increases in weight of 10–12%, was to place the swatch in 2.5 g. of maleic anhydride in 100 ml. of glacial acetic acid at 50° C. for 16 hr.

Ethyl Acrylate. This agent is expected to react with wool as follows:



Vinylation of wool, in this case by ester interchange, gave uptakes of 4–5% when carried out using basic and acidic catalysts. In general the experiments were carried out by placing each swatch in 100 ml. of dimethylformamide; to this was added 50 ml. of ethyl acrylate and 0.1 g. of potassium hydroxide. The solution was heated to 115° C. and maintained at this temperature for 3 hr. After thorough rinsing and drying a 3.9% increase in weight was observed. Pretreating the swatch by heating it to 110° C. in dimethylformamide for ½ hr., squeezing out the excess, then adding the swatch to 100 ml. of ethyl acrylate containing 0.15 ml. of sulfuric acid gave an uptake of 5.4%. Without pretreatment, the reaction carried out under the same conditions gave an uptake of 1.4%.

N-Carbamyl Maleimide. This reagent is assumed to react with wool as follows:



Fabric swatches were treated with 5.0 g. N-carbamyl maleimide in 150 ml. glacial acetic acid. An increase in weight of about 10.4% was observed after 16 hr. in a constant temperature bath at 50° C.

Glycidyl Methacrylate (GMA). Vinylation of wool by GMA may occur by reaction of the epoxy group with the side-chain amines and hydroxyl groups.

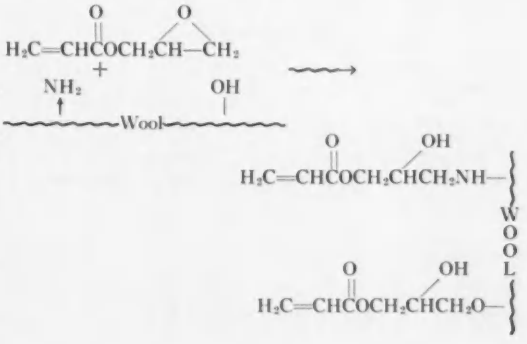
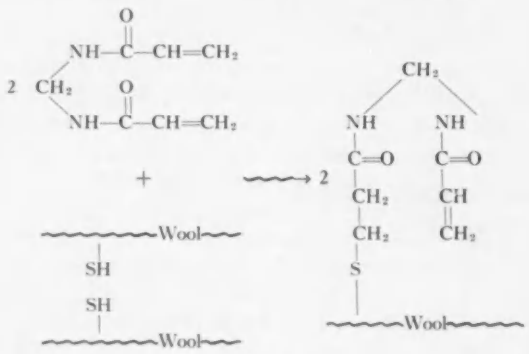


TABLE II. Alkali Solubility of Vinylated Wool

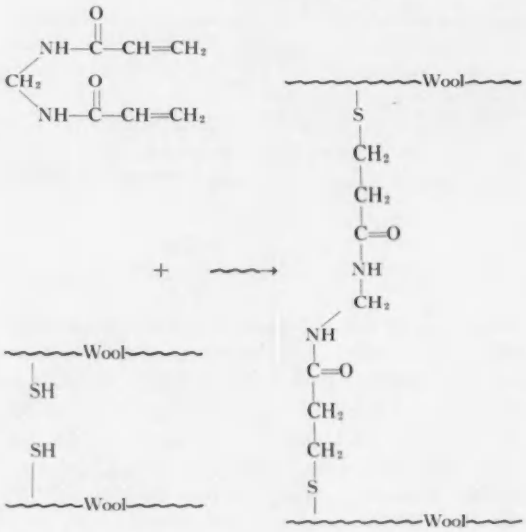
Sample no.	Treatment	Alkali solubility [3], %
1	Untreated	11.0
2	Ethyl acrylate	22.7
3	Acrylyl chloride	23.5
4	Maleic anhydride	26.4
5	Methylenebisacrylamide	1.8

Reaction with wool was attempted under various conditions. One procedure increased the weight up to 9.2%. This entailed heating the swatch in 130 ml. of toluene with 20 ml. of GMA and 0.1 g. aluminum chloride for 3 hr. at 110° C. (The possibility that this increase in weight was due to polymer formation was not eliminated.) The swatch was rinsed with toluene, 2-butanone, and finally water and then dried. In other procedure, the swatch was placed in 5 ml. GMA, 200 ml. of 0.1 *M* phosphate buffer solution, pH 6.1, and heated at 50° C. for 24 hr. Weight was increased 6.4%. Refluxing the swatches in a solution of GMA in acetone or carbon tetrachloride gave no increase in weight.

N,N'-Methylenebisacrylamide (MBA). The sulfhydryl groups of reduced wool may react with MBA to give a product in which two unreacted vinyl groups are introduced for each disulfide link reduced:



Another possibility is that a bisthioether bridge is formed in which the two sulfhydryl groups have added to the same molecule of MBA:



That the latter has occurred, to some extent, is indicated from the greatly decreased solubility of the treated swatches in alkali [3] as compared to the control and other vinylated samples (Table II). Further evidence in favor of cross-linking is found in a marked reduction of supercontraction (5% sodium bisulfite at 95° C.) of the treated fabric: 0–2% vs. 17% for the untreated fabric.

The treatment involves reduction of the wool with 0.5 *M* mercaptoethanol and heating in 150 ml. of 2% solution of MBA in water with 0.1 g. of sodium carbonate at 75–85° C. for 1 hr. After thorough rinsing and drying, the swatches had gained as much as 6% in weight.

Conclusion

Vinylated wools have been prepared by reaction of wool with acrylyl chloride, maleic anhydride, N-carbamyl maleimide, ethyl acrylate, and glycidyl methacrylate. By varying times, temperature, and solvent and reagent concentration, the degree of vinylation and the location of the vinyl groups in the wool can be controlled. With fiber-swelling solvents, such as water, acetic acid, and dimethylformamide, the reaction probably occurs throughout the entire fiber. With nonswelling solvents, reaction is assumed to be limited to the fiber surface. Both

surface-vinylated wool and wool vinylated throughout the fiber are of interest for use in graft polymer formation.

The vinylated wool is not visibly changed with the exception of the treatment with acrylyl chloride, which imparts slight yellowing, and the treatment with N-carbamyl maleimide, which imparts a slight pinkish cast.

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The Torsional Properties of Single Wool Fibers. Part II

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Abstract

Torque–twist and torsional relaxation tests on single wool fibers in water over the temperature range 7° C. to 44° C. show a rapid change with temperature. This change indicates that torsional properties are dependent upon a rate process mechanism. In a previous paper it was postulated that these properties can be explained in terms of a matrix in the wool fiber acting as a cross-linked polymer stabilized by a network of polar bonds. The drastic change in torsional properties of the wool fibers when the pH is changed from ~6.5 to 1.0 indicated that some of the bonds are salt-linkages: others will be hydrogen bonds. However, it is pointed out on the basis of the proposed model, that whereas the hydrogen bonds in the network can break and remake during mechanical deformation of the fiber, the salt-linkages on breaking apparently do not remake.

Introduction

In Part I of this series of papers [3] on the torsional properties of single wool fibers, the torque–twist and torsional relaxation properties of both wet and dry fibers were measured at room temperature and at a fixed rate of twisting. In this paper the authors report the results of measurements done within the temperature range of 7° C. to 44° C. An examination was made of the effect of changing the rate of twisting of the fiber both on the torsional rigidity and on the torsional relaxation at a fixed twist level. Further a comparison was made of both torque–twist and torque relaxation of the same fibers in distilled water (pH 6.5) and in hydrochloric acid solution of pH 1. Finally tests were carried out to determine the torsional properties of fibers which had been treated in thioglycollic acid at pH 5 and 37° C. to reduce disulphide bonds.

Due to the experimental difficulties involved in setting up each fiber for test, the number of fibers used in each test had to be limited. However, despite this limitation significant observations were made.

Experimental

A detailed account of the apparatus and techniques used in torsional measurements is given in Part I of this series of papers. It was found that, when the temperature of the water or glycerol in which the fiber was immersed exceeded the atmospheric temperature around the apparatus by 5° C., convection in the water or glycerol became excessive and interfered with the measurements of the fine torsion suspension used. For this reason the experiments were carried out in a small, temperature-controlled room, and the room temperature was

adjusted to the temperature of the experiment in hand.

In the experiments involving changes of the rate of twisting, the tests were confined to three speeds as before: 5.74 radians/min., 13.82 radians/min., and 24.4 radians/min. As mentioned in Part I, speeds in excess of 24.4 radians/min. were impractical because stirring of the liquid caused excessive disturbance of the torsion-measuring mechanism.

Results

Variation with Temperature

The torque–twist curves of single wool fibers in water for the temperature range studied (7°–44° C.) vary only in magnitude, the shape being the same as indicated in Part I. The curves approximate very closely to rectangular hyperbolae of the form[1]

$$\frac{1}{T} = \frac{a}{\theta} + b \qquad (1)$$

where T is the torque and θ the corresponding twist on the fiber under test. a and b are constants at constant temperature. Variation of temperature caused a rapid variation in the value of a, the slope of the curve $1/T$ vs. $1/\theta$. This is illustrated in Figure 1, which is a plot from experimental data of $1/T$ vs. $1/\theta$ at various temperatures for one fiber. Because of the relative inaccuracy of estimation of the value of b, it is not possible to say whether there is a real variation of this quantity with variation of temperature.

The values of the torsional modulus or rigidity for the five fibers tested at a number of temperatures are shown in Table I. The torsional modulus of a fiber decreased with increase of temperature. As a trial we may assume that the change with temperature proceeds according to the simplest rate-process equation; i.e. that

$$\eta = Ae^{E/R\tau}$$

where R is the universal gas constant, τ is the absolute temperature, E is defined as the activation energy, and A is a constant.

The plot of log η against $1/\tau$ should be linear. The results of Table I are not sufficiently comprehensive to demonstrate that the above equation is followed, but at least the data are consistent with such a mechanism over the temperature range used. Values of E obtained for each experiment were as follows: 3.5, 2.9, 4.6, 4.1, and 4.6 kg.-cal/mole. The mean value is 3.9 kg.-cal/mole.

The torque relaxation of fibers in water at a fixed value of twist, $\theta = 69.2$ radians, was obtained at several temperatures. The variation of torque with time is shown in Figure 2 for one of the fibers

[1] The equation $1/y = (a/x) + b$ may be rewritten as $(x + a/b)\ (y - 1/b) = -a/b^2$. This curve of y against x is a rectangular hyperbola asymptotic to the lines $y = 1/b$ and $x = -a/b$ and also passing through zero. Therefore if $1/y$ against $1/x$ is a straight line relationship, the relationship between y and x is a rectangular hyperbola.

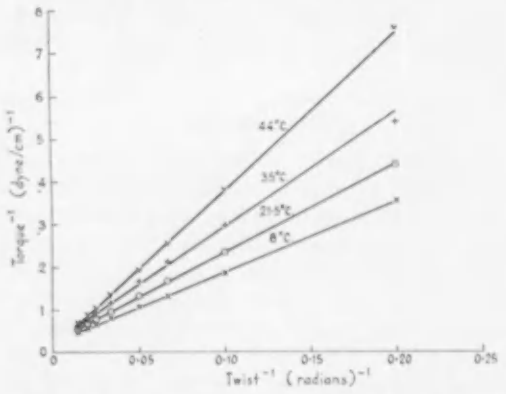

Fig. 1. The plot of inverse torque against inverse twist for a single wool fiber in water at four different temperatures.

TABLE I. Values of the Torsional Modulus of Five Wool Fibers in Water at Several Temperatures

Fiber	Temperature, deg. C.	Torsional modulus, dynes/cm.²
1	17.3	1.73×10^9
	31.6	1.42×10^9
	38.0	1.15×10^9
2	7.0	1.66×10^9
	19.0	1.42×10^9
	42.0	0.94×10^9
3	10.0	2.17×10^9
	13.0	2.12×10^9
	20.0	1.99×10^9
	41.0	1.00×10^9
4	8.0	2.19×10^9
	22.0	1.72×10^9
	35.0	1.32×10^9
	44.0	1.00×10^9
5	8.0	1.75×10^9
	22.0	1.27×10^9
	32.5	0.91×10^9
	42.5	0.75×10^9

TABLE II. Values of the Torsional Modulus of Four Wool Fibers in Water at Three Different Twist Rates

Fiber	Fiber diameter, μ	Torsional modulus (rigidity), dynes/cm.^{2}		
		5.74 rad./min.	13.82 rad./min.	24.4 rad./min.
P	39.2	1.33×10^9	1.61×10^9	1.92×10^9
Q	44.6	1.52×10^9	1.59×10^9	1.55×10^9
R	51.7	1.56×10^9	1.76×10^9	1.87×10^9
S	49.1	1.17×10^9	1.23×10^9	1.26×10^9

at four different temperatures. The torque T_t at time t min. is divided in each case by the torque T_{60} at time 60 min. Increase of temperature decreases the percentage torque relaxation in the time subsequent to 0.3 min. (As in Part I, time is measured from the instant that twisting ceases and torque relaxation has been proceeding during twisting. A point of interest here is that, irrespective of temperature, the torque in a fiber fell to approximately the same value at $t = 60$ min.)

The curves in Figure 2 of T_t/T_{60} vs. Log (t) at any fixed temperature do not vary significantly from fiber to fiber. The invariance of these curves at any fixed temperature explains the consistency of the values for three different fibers when $T_{0.3}/T_{60}$ is plotted against temperature (see Figure 3).

Torque–twist curves and torque relaxation curves were determined for fibers in analytical-reagent dry glycerol over the same temperature range (7°–44° C.) used in the experiments in water. Whereas in water torsional rigidity of a fiber over this temperature range varied by a factor of more than two to one (see Table I), in glycerol the change for the same temperature range was only between 10% and 20%. Similarly torque relaxation at constant twist in glycerol showed little variation with temperature. As an example one fiber gave a value of $T_{0.3}/T_{60} = 1.63$ at 8° C. and 1.58 at 43° C., a drop of 3%, whereas in water the values for the same fiber were 1.34 at 7° C. and 1.03 at 42° C., a change of 23%.

Variation with Rate of Twisting

Torque–twist measurements were carried out on single fibers in water at room temperature (20° C.) for the three rates of twisting indicated in the experimental section. Results for the four fibers tested in this manner are shown in Table II. There appears to be a general trend towards increase in the torsion modulus with increase in rate of twisting. However the results do not give a consistent change in the modulus with rate of twisting (compare fibers P and Q). Some of this inconsistency probably arises from the fact that the fibers are not constant-diameter cylinders and change in the rate of twisting may cause a change in the distribution of twist over the length of the fiber. The calculation of torsional modulus, being dependent on the fourth power of the diameter, may be affected considerably by such a redistribution of twist.

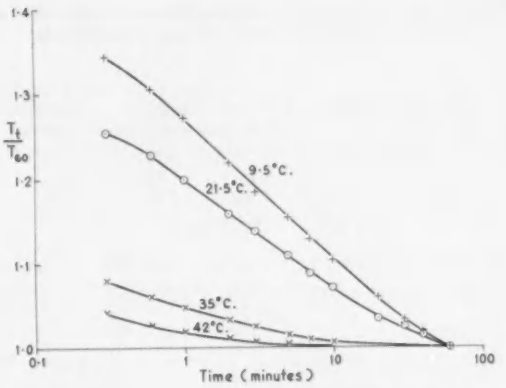

Fig. 2. The plot of T_t/T_∞ against log t for the torque relaxation of a single wool fiber held at a fixed strain in water at four different temperatures. T is the torque at time t after commencement of the experiment, T_∞ is the value of the torque corresponding to $t = 60$ min.

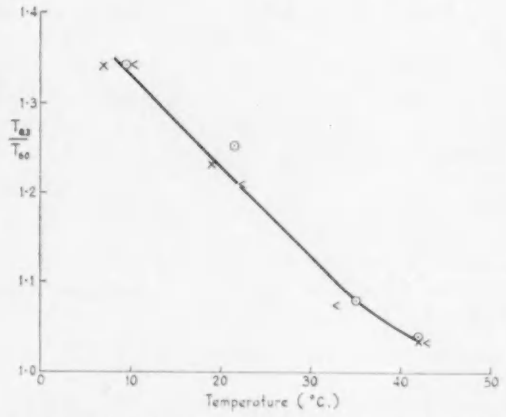

Fig. 3. The plot of $T_{0.3}/T_\infty$ against temperature for three wool fibers in water. $T_{0.3}$ is the value of torque corresponding to $t = 0.3$ min.

Torque relaxation at a fixed twist value, $\theta = 69.2$ radians, for these fibers in water was obtained for all the fibers after they had been twisted at the rates used in the above tests. These results were more consistent for variation of torque relaxation against twist rate than the values obtained for torsional modulus (see Table III). An increase in the rate

TABLE III. Values of the Torque Relaxation in Water of Three Wool Fibers at Three Different Twist Rates

Rate of twisting	Value of $T_{0.3}/T_{60}$		
	Fiber 1	Fiber 2	Fiber 3
5.74 rad./min.	1.24	1.21	1.18
13.82 rad./min.	1.26	1.24_5	1.22
24.4 rad./min.	1.30_5	1.27_5	1.24_5

of twisting results in an increase in the amount of torque relaxation in the time subsequent to $t = 0.3$ min.

Measurement at pH 1

Speakman and Hirst [4] have shown that mechanical properties of wool fibers in water are stable from pH 7 to pH 4. Between pH 4 and pH 1 the fibers are weakened but at pH 1 a new region of mechanical stability begins. This weakening [5] they thought due to breakdown of salt-linkages in the wool structure. Torque–twist measurements were carried out on the same fibers in water (~ pH 6.5) and in an unbuffered aqueous solution of HCl at pH 1. The curves at pH 1 were, as for water, rectangular hyperbolas, expressible in the form of Equation 1. The value of the rigidity modulus is reduced at pH 1 to about 38% of the rigidity modulus in water at ~ pH 6.5.

However, whether the fiber is at pH 1 or pH 6.5, the value of b in Equation 1 is unchanged (see Figure 4).

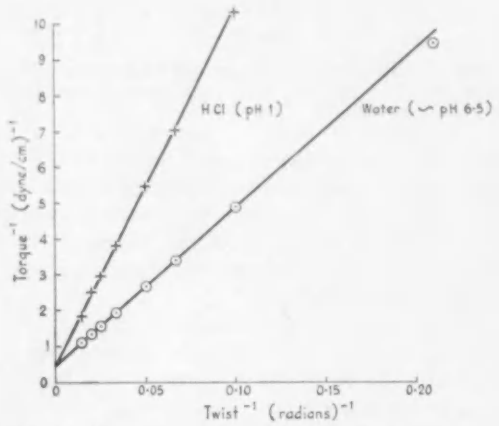

Fig. 4. The plot of inverse torque against inverse twist for a single wool fiber in water and in an aqueous solution of HCl at pH 1.

Torque relaxation at a fixed value of twist of 69.2 radians was compared for the same fibers at pH 1 and at ~ pH 6.5. The proportion of relaxation is considerably reduced at pH 1, the value of $T_{0.3}/T_{60}$ being reduced significantly from a mean of 1.26 at ~ pH 6.5 to 1.16 at pH 1 (a value of $T_{0.3}/T_{60} = 1$ would indicate no relaxation subsequent to $t = 0.3$ min).

Thioglycollic Acid Treated Fibers

Three fibers were tested from two batches treated in thioglycollic acid pH 5 and 37° C.—one from Batch A and two from Batch B. Batch A was treated for 3½ hr. and showed on analysis a reduction of 37% in the cystine content. The other batch was treated for 21 hr. and showed a cystine loss of 53%. The major part of the cystine breakdown is due to a conversion of cystine to cysteine. The three fibers showed torque–twist and torsional relaxation properties in water significantly different from normal wool fibers (see Table IV). However no significant difference, on the basis of these three fibers, seems to exist between Batches A and B despite the indicated difference of cystine content. This result is in accord with previous observations [2] on the supercontraction behavior in concentrated LiBr solutions of fibers taken from Batches A and B.

Discussion

The rapid change of the rigidity of the wool fiber in water over the temperature range 7° C. to 44° C. and the corresponding rapid change of torque relaxation both point to the value of the torque in the fiber being dependent on a rate process involving the increase in breakdown of strained bonds with increase of temperature. The changes of rigidity and torque relaxation with rate of twisting also are compatible with a rate process mechanism. For the dry fiber (in glycerol), however, the changes with temperature of the torsional properties of a single wool fiber are negligible when compared with the effects in water. This suggests that the bond breakdown involved in the rate process mechanism is due to polar bonds such as hydrogen bonds and salt-links, which are affected by the presence of water.

In the previous paper on torsional properties of single wool fibers, it was proposed that the matrix, on which the torsional properties mainly depend, may be considered as a cross-linked polymer stabil-

TABLE IV. Variation of the Rigidity Modulus and Torque Relaxation for Untreated and Thioglycollic Acid Treated Wool Fibers in Water

	Normal untreated fiber	Fiber 1, Batch A	Fiber 2, Batch B	Fiber 3, Batch B
"η" the torsional rigidity (wet), dynes/cm.^{2}	1.61×10^9	1.28×10^9	1.01×10^9	1.29×10^9
$T_{0.3}/T_{60}$	1.27	1.80	1.88	1.99

ized by a network of hydrogen bonds. In this picture the rigidity is due chiefly to the straining of the hydrogen bonds in the network. Further, the asymptotic value of the torque for a fiber in water is due to the breaking and reformation of hydrogen bonds. The results of the torsional measurements at pH 1 as against ~ pH 6.5 indicate that the rigidity of the fiber results from the straining not only of hydrogen bonds, but also of other polar bonds such as salt-links, the latter being purely ionic bonds. However the asymptotic value of the torque in the torque–twist curve shows little change from pH 6.5 to pH 1 (Figure 4) indicating that the bonds being broken and reformed have very little ionic component. This means that it must be hydrogen bonds with a relatively small ionic component that are breaking and remaking and controlling the asymptotic value of the torque in the torque–twist curve. It appears that the picture of the matrix as a cross-linked polymer stabilized by a network of hydrogen bonds must now be extended to include salt-linkages in the network. However these linkages, when broken by strain, apparently show no tendency to remake on new sites and hence do not contribute to the asymptotic value of the torque in the torque–twist curve. The lower amount of torque relaxation at pH 1 as against ~ pH 6.5 also indicates that the breakdown under strain of salt-linkages plays a large part in the torque relaxation mechanism at ~ pH 6.5.

It is also interesting to note that the rigidity at pH 1 is about 0.4 of the rigidity at pH 6.5. In measurements of linear mechanical properties carried out by the authors [1] on wool fibers, the change over the same pH range was not quite as drastic as the change in the rigidity. For example, the force at 15% extension at pH 1 is 0.6 of the force at ~ pH 6.5. This fact can be interpreted to mean that salt-linkages play a greater part in the mechanical stability of the matrix than they do in the whole fiber.

The effect on torsional properties produced by reduction of part of the cystine with thioglycollic acid indicates, just as in supercontraction behavior [2], a drastic change produced only by the removal of the first fraction of cystine links. This change may be essentially configurational, rather than reflecting change of cystine content. However without further investigation little can be concluded except to note the nature of the mechanical change produced.

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Some Aspects of the Reaction between Urea and Cellulose[1]

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Abstract

A reaction occurs between cellulose and urea when cellulose and an aqueous solution of urea are heated to an elevated temperature. Evidence for reaction are (1) insolubility of the treated cellulose in cupriethylenediamine, (2) changed infrared absorption spectrum, (3) nitrogen content unaffected by boiling water, (4) changed dyeing properties, and (5) modified moisture regain. There is no change in the cellulose X-ray diffraction pattern, and all of the original cellulose properties are restored by boiling in 2% caustic solution. The urea treatment does not affect the textile properties of cotton fabric. Biuret also reacts with cellulose giving a product having the same properties as the material treated with urea.

UREA has been used in cellulosic textile finishing for quite some time but always in combination with another chemical for bestowing such properties as crease resistance, flame resistance, water repellency, better dyeing, and the like. Detailed reviews of several of these processes have been made by Wardle [16] and others [15]. Other than the work of Preston and co-workers [10], who applied urea solutions to cellulose fibers to study swelling effects, there seems to be little reported data on any studies of urea used alone as a cellulosic textile modifying agent.

Nuessle [6], however, in some unpublished data showed that cotton fabric, immersed in a 50% urea solution containing 1% cupric chloride as a catalyst, dried, and cured at elevated temperature, gave a "cellulose carbamate" containing from 1.5% to 2.25% nitrogen. The nitrogen content of the reaction product was increased either by raising the curing temperature or lengthening the time of cure. He stated that almost twice the nitrogen content was obtained with rayon as with cotton, which in his opinion indicated that the extent of the reaction with cellulose was determined by the accessibility of the cellulosic hydroxyl groups. In spite of there being a reaction with urea, however, he claimed that it brought about no marked improvement in textile properties.

Fisher [3] made a study of the effect of urea and substituted ureas on the mechanical properties of paper. Pulp handsheets were merely soaked in solutions of the compounds, and the sheets air dried. Fisher found that such treatments reduced the tensile strength and elastic modulus of the sheet while increasing its ability to flow under stress. He ascribed the effects to a state of dry swelling where the cellulose chains were mechanically separated by the presence of the additive molecule in the cellulose structure.

According to patents held by Schreiber [14] and by Hill and Jacobson [4], wood pulp and linters were reacted at elevated temperature with urea and a sodium hydroxide catalyst. Since these workers had no definite knowledge of the nature of the reaction products, they designated them as "urea celluloses" or "cellulose carbamates." These products were stated to contain 1–2.5% nitrogen and to be soluble in cold dilute caustic. These workers claimed that impregnated pulp became soluble only after baking at 120–150° C., which was interpreted to mean that reaction between the urea and cellulose took place in the substantially dry state during the baking. However, baking a urea-impregnated sample at 170° C. without the sodium hydroxide catalyst was said to result in an insoluble product, while immersion in molten urea at 155–160° C. was ef-

[1] Presented before Division of Cellulose Chemistry, American Chemical Society, New York, N. Y., September 12–16, 1960.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

fective in preparing a soluble one. The alkali-soluble "urea celluloses," stated to be useful for casting film, for spinning filament, and for sizing textiles and paper, were coagulated by use of solutions of acids or salts or by organic solvents.

The present investigation was undertaken in an attempt to get some information on the cellulose-urea reaction product and on the conditions under which the reaction product is formed.

Materials and Methods

The sources of cellulose for this study were a kier-boiled, singles cotton yarn, a bright, unfinished viscose rayon yarn, and a scoured, 80 × 80 cotton print cloth. A portion of the cotton yarn was treated with sodium hydroxide solution to produce the cellulose II crystal modification, while another portion was treated with anhydrous ethylamine to produce the cellulose III modification.

Of the chemicals used in this study, urea, monomethylurea, 1,3-dimethylurea, and biuret were of reagent grade, while the ethyleneurea was technical grade material that was highly purified by recrystallization from isopropanol. The purity of all the compounds was checked by analysis and their infrared spectra were obtained.

Samples were treated with 50% aqueous solutions of urea and substituted ureas and 12% biuret dissolved in dimethylformamide in the following maner. The sample was immersed in the solution for 1 hr.; then the wet pick-up was adjusted to 100%. The impregnated sample was placed in a forced-draft oven at 170° C. for 2 hr. After curing, the sample was boiled for 1 hr. in 2 changes of boiling distilled water to remove unreacted materials. Percent dry pick-up was obtained after air drying. In one set of treatments with aqueous urea the treating conditions were varied: 12½%, 25%, and 50% solutions were used with curing temperatures of 140°, 155°, and 170° C., and curing times of ½, 1, and 2 hr.

Not only because had Nuessle [6] expressed the view that the cellulose-urea reaction was actually one between cellulose and molten urea, but also because of the claim of Hill and Jacobson [4] that pulp immersed in molten urea became alkali soluble, several experiments were carried out with molten urea. Samples were immersed for 4 hr. in molten urea held at 145° C., then extracted in a Soxhlet apparatus with isopropanol until free of unreacted material. In another experiment, however, the melt was held at 170° C. with a sample immersion time of 2 hr. followed by extraction with water.

Nitrogen contents of the treated celluloses were determined by the Kjeldahl method. The infrared spectra were obtained using the potassium bromide disc technique and the apparatus and procedure described by O'Connor and co-workers [7].

Moisture regain of untreated and treated samples was measured by approaching from the dry side. One-gram samples were dried for 3 hr. at 105–110° C., then placed in an atmosphere of 65% RH (over saturated sodium nitrite solution held at 70° F.) to equilibrate. Final drying took place overnight at 105–110° C.

The treated celluloses were observed for solubility in cupriethylenediamine (CED) by a microscopic technique. A few fibers from a yarn were placed on a microscope slide under a cover glass and observed through the microscope while 2 to 3 drops of 0.5 *M* CED were introduced under the cover glass. If the fibers failed to dissolve after 15 min., they were considered to be insoluble. The quick test had been checked by permitting larger samples to stand overnight in an excess of the reagent.

Results and Discussion

Application of Urea

The data given in Table I, except for that in the column for molten urea, confirm the information furnished by Nuessle [6]. Impregnated cotton and viscose cellulose did react with urea when heated, yielding nitrogen-containing materials stable to boiling water, while incorporation of a metal halide salt in the urea solution did strongly increase the amount of nitrogen fixed by the cellulose. The amount of nitrogen in treated viscose rayon was almost double that in cotton cellulose I which is probably due, as claimed, to the greater accessibility of the viscose cellulose. This view is supported by the higher nitrogen contents of the treated cotton celluloses II and III. Both of these crystal modifications are also known to have accessibilities different from that of cotton cellulose I. The insolubility in CED of the products with high nitrogen content was unexpected. This effect, however, may be taken as an indication that reaction with the cellulose has taken place instead of there being a mere deposition of polymeric material on and in the fiber. The reaction may or may not be one of cross-linking. Reeves [13] has shown that blocking of either or both of the 2,3 hydroxyl

TABLE I. Nitrogen Contents of Urea-Treated Materials

Material	Untreated, %	Treated in molten urea, 4 hr. at 145° C., %	Impregnated with 50% aqueous urea, cured 2 hr. at 170° C., %	Impregnated with 50% aqueous urea containing 1% cupric chloride, cured 2 hr. at 170° C., %
Cellulose I	0.03	0.26*	1.24†	2.27†
Cellulose II	—	0.57*	1.73†	3.00†
Cellulose III	0.05	0.47*‡	1.76†	3.06†
Viscose	0.006	0.95*	3.52†	4.88†
Glass fabric	0.00	0.00	0.00	0.00

* Soluble in CED.
† Insoluble in CED.
‡ A sample of cellulose III held 2 hr. in molten urea at 170° C., extracted with water, contained 0.80% nitrogen and was soluble in CED.

groups in glucosides and in cellulose is enough to prevent complex formation with a copper-containing cellulose solvent and to prevent cellulose from dissolving in the solvent. Cyanoethyl cellulose with a degree of substitution of 1 or more, where cross-linking is known not to exist, is extremely resistant to dissolution in CED. Comparison of the X-ray diffractograms of untreated and urea-treated materials showed no changes in the crystalline interferences, which suggests that the reaction occurs only in the amorphous or accessible regions of the cellulose and that the crystalline regions are unaffected.

The low nitrogen content of the cellulose treated with molten urea, and the solubility of the treated samples in CED, particularly the latter, suggest that little or no reaction has taken place between cellulose and urea under these conditions.

The curves shown in Figure 1 are the infrared spectra of untreated and urea-treated cellulose I and viscose rayon. According to O'Connor and co-workers [8] chemical modification of cotton fiber can be readily detected and identified, and the extent of treatment can be quantitatively estimated from the infrared absorption spectra. In this case, however, identification cannot be made very satisfactorily because the spectra are lacking enough new bands for positive identification and assignment. A similar condition was reported by O'Connor and co-workers [7] for phosphorylated and sulfoethylated cottons. In the urea-treated celluloses there are only three new absorption bands, a medium to strong one at 5.80μ, a weak one at 6.20μ, and a very weak one at 12.9μ. The new weak band at 6.20μ cannot be readily assigned, but the one at 12.9μ probably arises from an N-H deformation. The new band at 5.80μ would normally arise from a carbonyl group, but seems to vary in intensity according to nitrogen content of the treated cellulose. Whether this carbonyl absorption comes from an ester, a diacylimide, a urethane, or an amide group in the cellulose cannot be definitely decided solely from the infrared data presently at hand. The presence of these bands in the spectra of the celluloses treated with molten urea and which were soluble in CED makes this all the more difficult to interpret. For example, in Figure 2 the intensity of the 5.80μ band of the cellulose II treated with molten urea at 170° C. is almost identical to that of the sample treated with aqueous urea. The two spectra are almost identical. But the nitrogen content of the former, soluble in CED, is only 0.8%, while that of the latter, insoluble in CED, is 1.6%.

Experiments where variations were made in solution concentration, curing temperature, and curing time gave the nitrogen data shown in Table II. Although the nitrogen contents were fairly reproducible in repeat experiments, plotting the data in various ways failed to show any trends in concentration, time, or temperature that would be of fundamental significance. The more concentrated solution produced the highest nitrogen content, which was the same, 1.61–1.67%, whether 155° C. or 170° C. curing temperature was used, or 1 or 2 hr. curing time. Lower concentrations were also fairly consistent in this respect. Higher nitrogen concentrations could have been attained with a catalyst, but

it was thought that the presence of a catalyst might complicate the picture. All of the samples, except the two indicated by an asterisk in the table, were insoluble in CED. The increased sample weight arising from nitrogen-containing material in the fiber showed only a general trend in relation to nitrogen content as shown in Figure 3. The scatter of the data seems to suggest that the reaction product may not be one formed in stoichiometric proportions but may contain a mixture of products. On the other hand, as shown in Figure 4, a regular increase in intensity of the 5.80μ carbonyl absorption band seemed to accompany increasing nitrogen content. This relationship would suggest that the carbonyl group may be a structural part of the nitrogen-containing portion of the reaction product.

The data in Table III show the moisture regains for those samples whose nitrogen contents are given

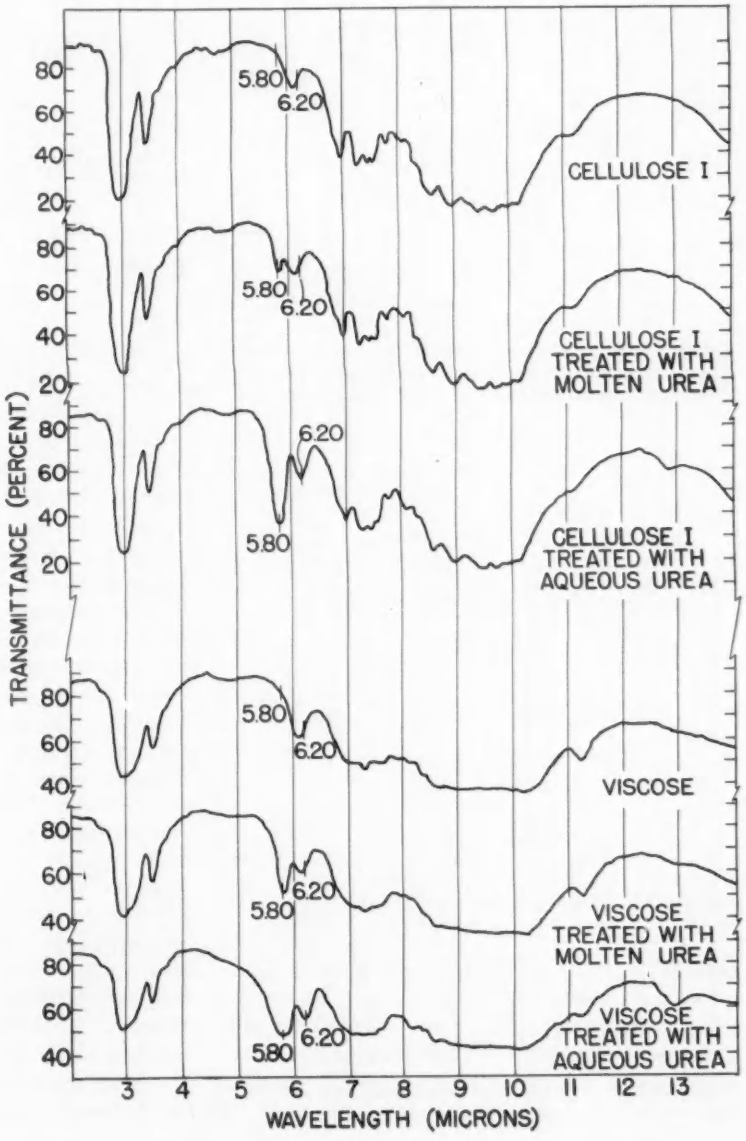


Fig. 1. Infrared spectra of untreated and urea-treated cellulose I and viscose rayon. (Molten urea at 145° C.)

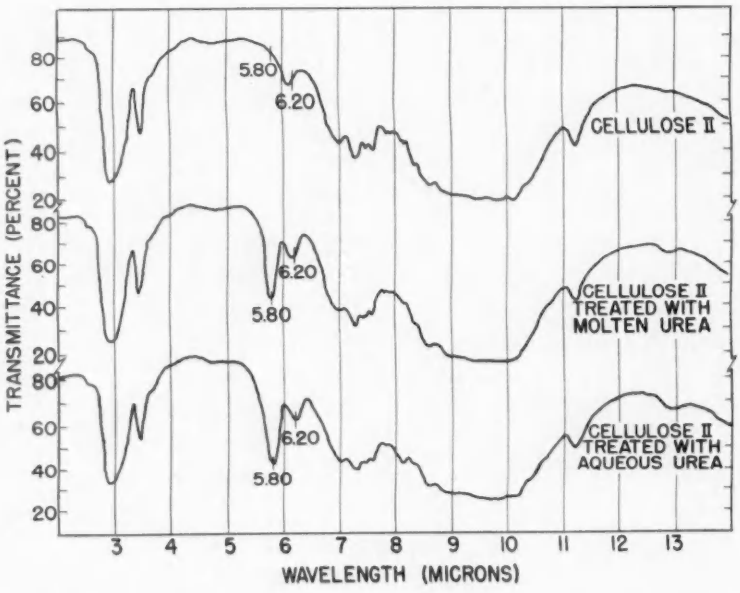


Fig. 2. Infrared spectra of untreated and urea-treated cellulose II. (Molten urea at 170° C.)

TABLE II. Effect of Varying Solution Concentration, Curing Temperature, and Curing Time on the Nitrogen Content of Cellulose Treated with Aqueous Urea without a Catalyst

Urea solution concentration, %	Nitrogen content in percent		
	Curing temperature		
	170° C.	155° C.	140° C.
	2 hr. curing time		
50	1.61	1.62	1.22
25	1.14	1.05	0.91
12.5	0.84	0.82	0.70
	1 hr. curing time		
50	1.67	1.61	0.75
25	1.12	0.93	0.63
12.5	0.82	0.75	0.51
	½ hr. curing time		
50	1.27	1.01	0.55
25	1.08	0.74	0.29*
12.5	0.75	0.54	0.30*

* These two samples were soluble in CED. A sample impregnated with 37.5% urea and cured ½ hour at 140° C. contained 0.39% nitrogen and was insoluble in CED.

in Table II. The regain data present what appear to be two anomalies. First, the regains of the treated samples range from lower than to greater than that of the untreated cellulose sample. Second, when plotted the data are prevented by various masking effects from showing any basic trend in relation to nitrogen content. It is possible that both are the result of the effect of swelling of the fiber by the urea solutions prior to curing. Preston and co-workers [10] found that 15.5% and 30% aqueous urea solutions applied to cotton caused increases in volume swelling of about 24% and 45% over that of water-swollen fiber. The moisture regain and accessibility of a swollen cellulosic fiber are usually greater than that of an unswollen fiber, while a reduction in regain is usually observed after heating at elevated temperature or after chemical reaction. In the current data, the low regain observed in the samples treated with 12.5% urea solutions apparently arises because this concentration is not of sufficient strength to cause swelling great enough to overcome the effect of heat and reaction. With 25% solution, however, regain is essentially unchanged from that of the untreated cellulose. This could come about if the effect of swelling almost balanced the effect of other treatments restricting the sorption of water vapor. A high degree of swelling, overcoming the effect of other treatments, would cause a high regain. This would be the case for the 50% urea solution, where the highest regains are observed. In plotting the data, moisture regain was found to vary more consistently with urea solution concentration than with nitrogen content. Although fiber cross-sections of the treated fibers examined

under the microscope did not show any significant increase in fiber diameter arising from the treatment, this would not necessarily reflect the accessibility of the cellulose to water vapor.

In spite of high moisture regain, the dyeing behavior of a sample treated with a 50% solution (the cellulose containing 1.67% nitrogen and insoluble in CED) presented what is usually accepted as one indication of a cross-linked cellulose—a high degree of dye resist to a direct cotton dye, Solantine Fast Blue 4GL. Dye resistance, however, could result also from the presence of substituent groups on the cellulose chain which would prevent binding of the dyestuff in the normal manner. Although the treated cellulose had a high nitrogen content, it dyed no differently from untreated cotton with an acid wool dye, Cloth Fast Red BR. Lack of dyeing with the acid dye would suggest that there are no basic nitrogen-containing groups in the reaction product; this was also indicated by titration of the product with standard hydrochloric acid. Calco Indentification Stain No. 2, used for determining the nature of undyed fibers, produced in the sample a pink coloration similar to that given to filament nylon. Untreated cotton is dyed green by this stain. The reaction to the stain might arise from a high degree of accessibility in the treated fiber, but it could possibly arise also from the presence of a substituted amide group, —NH—C—, a group which is found in nylon.

The nitrogen-containing groups in the treated fiber were not resistant to boiling dilute caustic solution. Samples containing 1.37% nitrogen and insoluble in

TABLE III. Moisture Regain of Cellulose Treated with Aqueous Urea under Various Conditions of Concentration, Curing Time, and Curing Temperature

Urea solution concentration, %	Moisture regain in percent*		
	Curing temperature		
	170° C.	155° C.	140° C.
	2 hr. curing time		
50	7.66	7.16	7.12
25	7.07	6.76	6.91
12.5	6.83	6.55	6.69
	1 hr. curing time		
50	7.57	7.40	7.09
25	6.80	6.80	6.96
12.5	6.49	6.62	6.76
	½ hr. curing time		
50	7.66	7.31	7.27
25	6.82	6.96	7.01†
12.5	6.59	6.72	6.90†

* Moisture regain of untreated cellulose sample—6.87%.
† These samples were soluble in CED.

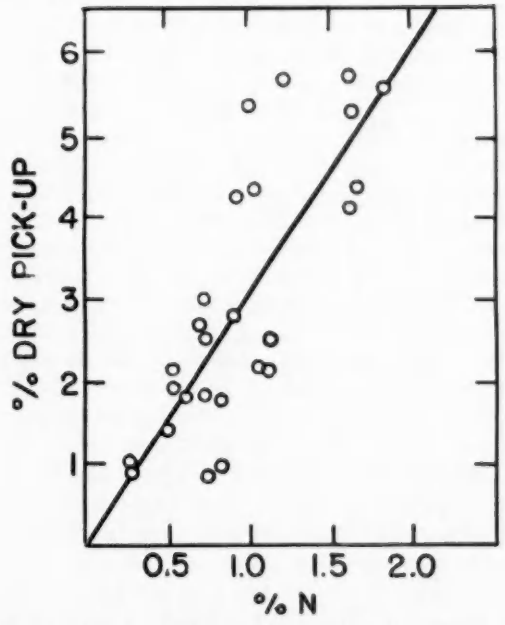


Fig. 3. Relationship between increased sample weight and nitrogen content after reaction with urea.

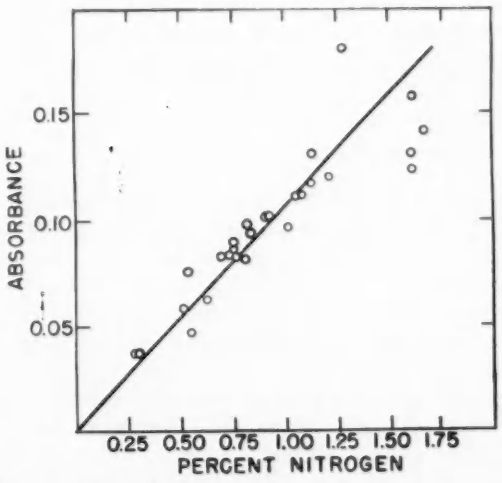


Fig. 4. Increase in intensity of the 5.80 μ carbonyl band with nitrogen content.

CED were reduced to 0.05% nitrogen by a 30-min. exposure to a boiling 2% solution of sodium hydroxide. Solubility in CED was restored completely. The infrared spectra of the samples after the alkaline boil showed a complete absence of the peaks at 5.80μ and 6.20μ, so that the spectrum was identical with that of the original untreated cellulose. The dyeing behavior of the sample after the alkaline boil was the same as that of the untreated sample—it dyed to the same shade with the direct cotton dye, Solantine Fast Blue 4GL.

The data in Table IV confirm Nuessle's [6] claim that there was no marked improvement in textile properties as a result of the reaction with urea. The slight changes in stiffness and in crease recovery are of no great importance. The only sizable change is the 50% reduction in tear strength. Consideration of the textile data along with the insolubility in CED, dyeing behavior, and moisture regain of the treated cellulose leads to the conclusion that little, if any, cross-linking has occurred, but rather a more accessible, substituted cellulose has been produced by reaction with urea. The question still remains, however, as to what the reaction product or products may be.

TABLE IV. Properties of an 80 × 80 Cotton Print Cloth before and after Treatment with 50% Aqueous Urea and 1% Cupric Chloride Catalyst

(2 hr. cure at 170°C.)

	Untreated sample	Blank sample	Sample treated with urea
% nitrogen	—	—	1.9
Solubility in CED	Soluble	Soluble	Insoluble
Breaking strength, lbs., warp	37.5	39.7	34.4
Breaking strength, lbs., fill	27.4	25.2	24.3
Elongation, %, warp	7.3	7.6	7.7
Elongation, %, fill	11.7	13.4	12.0
Tear strength, gm., warp	1089	667	520
Tear strength, gm., fill	726	427	307
Crease recovery, degrees, warp	86.3	82.3	105.3
Crease recovery, degrees, fill	85.0	80.3	102.7
Stiffness, in.-lbs., warp	5.2×10^{-4}	4.3×10^{-4}	3.6×10^{-4}
Stiffness, in.-lbs., fill	1.7×10^{-4}	2.3×10^{-4}	2.2×10^{-4}
Thread count, warp	80	82	82
Thread count, fill	76	80	77

Application of Substituted Ureas

The substituted ureas, monomethyl-, 1,3-dimethyl-, and ethyleneurea, were applied to cellulose under the same conditions as those used with urea in order to obtain data which might be helpful in determining the composition of the urea-cellulose reaction product. When heated above the melting point, urea decomposes with loss of ammonia to form cyanic acid, HN=C=O, which reacts with alcohols to give carbamates, $H_2N-\overset{\overset{O}{\|}}{C}-OR$, and dimerizes to form dicyanic acid, $H_2NCONHCOOH$, which reacts with alcohols to form allophanates, $H_2NCONHCOOR$ [2]. It is possible that cyanic acid from the decomposition of urea, and some dicyanic could react with the cellulose hydroxyls under the conditions of the urea treatment. Jacobson and others [5] have found that merely refluxing a solution of urea in an alcohol, at temperatures below the melting point of urea, produces carbamates. The lower boiling alcohols, methyl and ethyl, however, had to be reacted in sealed tubes to cause the reaction to take place.

Monosubstituted ureas decompose on heating giving ammonia and isocyanates, the latter react with alcohols to give N-substituted carbamates. Methyl isocyanate from monomethylurea would form a cellulose N-substituted carbamate. Neither 1,3-dimethylurea nor ethyleneurea decompose on heating, therefore no reactive compound would be present.

Considering the urea-cellulose reaction along these lines then, it would seem that cellulose treated with substituted ureas which cannot form cyanic acid or isocyanates should exhibit little or no evidence of reaction. The data in Table V and the infrared spectra in Figure 5 suggest that this proposition may be valid. Only the monomethylurea-cellulose product contains appreciable nitrogen and lacks complete solubility in CED. The spectrum of the product shows, in addition to the cellulose absorptions, a significant absorption peak in the 5.8μ region and a weak absorption band at 6.20μ. This spectrum is almost identical to that of a urea-treated cellulose. The sample treated with ethyleneurea, on the other hand, contains only a small amount of nitrogen and is completely soluble in CED. Its infrared spectrum is very similar to that of untreated cellulose.

Although the 1,3-dimethyl urea was indicated by analysis to be of high purity and gave a cellulose reaction product of low nitrogen content, the infrared spectrum of the reaction product displays weak absorptions in the 5.8μ and 6.2μ regions. The presence of a small impurity of 1,1-dimethylurea in the 1,3-dimethylurea could cause these results.

Application of Biuret

In the thermal decomposition of urea, the cyanic acid which is formed further reacts in the urea decomposition system to form biuret and several other products. Redemann and co-workers [12] have shown that heating anhydrous urea for 2 hr. at 140° C. converts some 7% of the urea to biuret, and that 14% of the urea is converted when heated at 170° C. for 1 hr. Therefore, the possibility of biuret being formed within the fiber during the urea treatment cannot be ignored.

Biuret is fairly soluble in boiling water, and the leaching step after curing could remove a significant amount of any which might be formed in or on the fiber. In the urea treatment, tests for biuret made on leach water were negative, showing that no biuret was extracted from the treated fiber. If biuret was formed in the curing step—and the conditions are right for its formation here [12]—the biuret either reacted with the cellulose, further changed into some other compound which reacted with the cellulose, or was somehow removed during the curing operation. Infrared data (Figure 6) also suggested that biuret as such was not present in the cellulose. In the spectra of untreated cellulose and of the reaction product, the bonded —OH absorption in the 3μ region and the —CH_2 stretching mode near 3.5μ failed to show any significant differences in shape or intensity, although the bonded —NH_2 stretching of biuret in the 3μ region is very intense and sharp. The two broad, very intense absorption peaks of equal intensity in the biuret spectrum, one with maximum at about 5.85μ and the other at 6.25μ (the carbonyl and amide absorptions), coincide with absorptions at those regions in the spectrum of the treated cellulose, but the intensities of the two peaks in the latter spectrum are far from equal. Other absorptions in the biuret spectrum which should be superimposed on the cellulose contribution to the spectrum are absent. All this can be seen by comparing the curves in Figure 6.

TABLE V. Nitrogen Contents and CED Solubilities of Cellulose Treated with Substituted Ureas in 50% Aqueous Solution Containing 1% Cupric Chloride Catalyst

(2 hour cure at 170° C.)

Substituted urea used	% Nitrogen in product	CED solubility of product
Monomethylurea	1.36	Partial
1,3-dimethylurea	0.48	Soluble
Cyclic ethyleneurea	0.50	Soluble

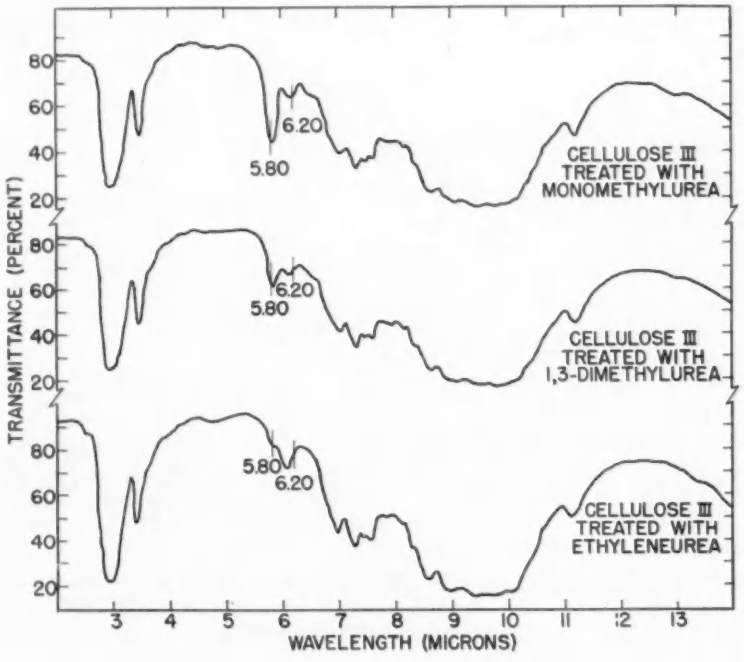


Fig. 5. Infrared spectra of cellulose III treated with monomethylurea, 1,3-dimethylurea, and ethyleneurea.

The apparent absence of biuret was investigated by substituting biuret for urea in the urea treatment of cellulose. Because of its poor solubility in water, the biuret was dissolved in dimethylformamide to give a 12% solution (saturated) at room temperature. It was not known whether reaction with the cellulose would take place, although Bishop [1] found that refluxing biuret and *n*-butyl alcohol for a short time yielded a mixture of carbamic and allophanic esters. Analysis of the cellulose after treatment disclosed a nitrogen content of 1.19%. The product was insoluble in CED and showed a dye resist to the direct cotton dye every bit as great as that of the urea reaction product. Interestingly enough, a negative biuret test was obtained on the leach water from this treated yarn also. The infrared spectrum of the biuret-cellulose reaction product, shown in Figure 6, is clearly almost identical to that of the urea-cellulose reaction product. This indicates that in the urea and biuret treatments the same product or products are formed with cellulose under the conditions of the treatment. The biuret-cellulose product was also similar to the urea-cellulose product in another respect—exposure to a

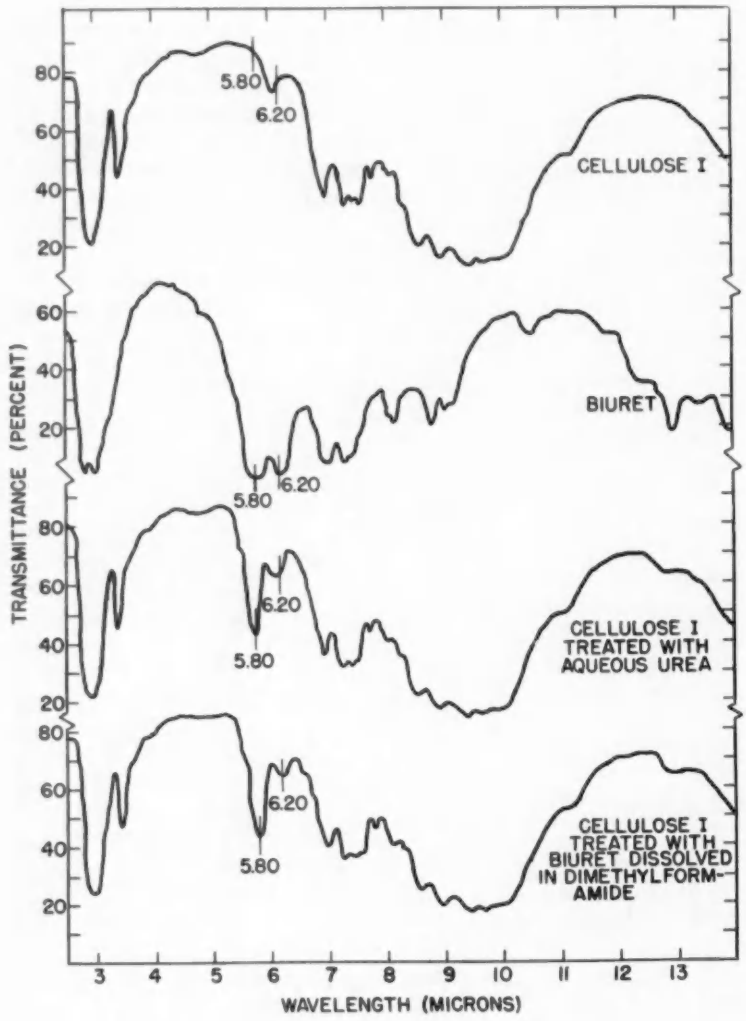


Fig. 6. Infrared absorption spectra of cellulose, biuret, urea-treated cellulose, and biuret-treated cellulose.

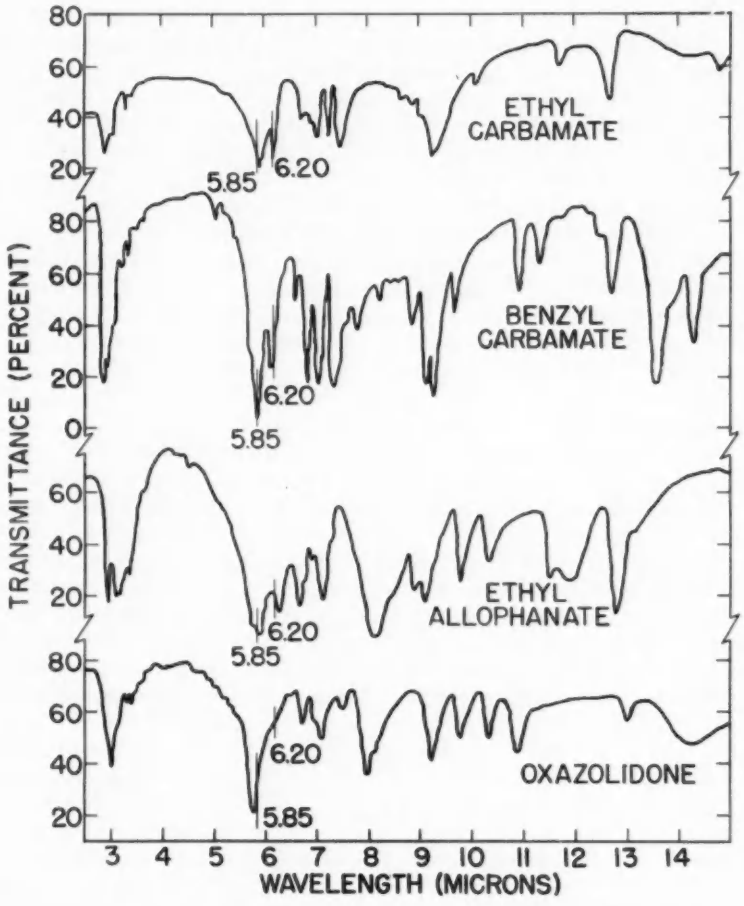


Fig. 7. Infrared absorption spectra of ethyl carbamate, benzyl carbamate, ethyl allophanate, and oxazolidone.

30-min. boil in 2% sodium hydroxide solution reduced the nitrogen content to 0.07%, restored complete solubility in CED, regenerated affinity for the direct cotton dye, and reestablished the cellulose infrared spectrum.

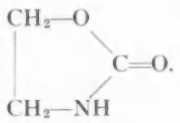
Consideration of the Nature of the Reaction Product

The principal product from heating urea or biuret with an alcohol has been shown to be an ester of carbamic acid [5, 1] the yield of which was greatly increased by lengthening reaction time. The true reactant with the alcohol, however, was not urea or biuret, but cyanic acid formed in the thermal decomposition of these compounds. Since the conditions used in the present work for treating cellulose with urea are favorable for the formation of cyanic acid, it is likely that the reaction product may be predominantly cellulose carbamate. Because of this possibility, the infrared spectra of ethyl and benzyl carbamates were obtained and studied. As can be seen in Figure 7, the spectra of both of these carbamates display a strong, sharp absorption peak in the 5.85–5.9μ region and a weak one in the region of 6.15–6.20μ. These peaks correspond very closely in location and relative intensity to similar ones in the spectra of the cellulose products. The 5.9μ absorption has been assigned to a joint ester-amide carbonyl group and the 6.2μ mode to the amide I band [11]. Although the rest of the carbamate absorptions in the 7–9.5μ region are lacking in the spectra of the cellulose reaction products, these could be masked by the strong absorption of cellulose in this region. This effect of the cellulose absorption in this region has already been pointed out by

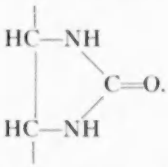
O'Connor and co-workers [8]. The $—NH_2$ stretching absorption of the carbamates in the 2.9μ region would also be masked by the strong, broad —OH stretching mode of cellulose in the same region.

Another product which has been obtained in heating an alcohol with urea or biuret is the ester of allophanic acid, the dimer of cyanic acid. The allophanic ester is formed along with the carbamic ester in the reaction, but its concentration rapidly lessens as reaction time is lengthened [5, 1]. This fact alone would suggest that little, if any, cellulose allophanate would be formed in the urea-cellulose reaction. The absorptions observed in the infrared spectrum of ethyl allophanate (Figure 7), however, does not exclude the presence of some allophanate in the cellulose reaction product, although from the relative intensities of the absorption peaks one would expect more than the 5.9μ and 6.2μ peaks to appear in the spectrum of the reaction product if this grouping were present.

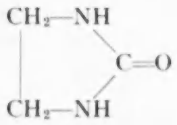
Since the hydroxyl groups on the number 2 and 3 carbon atoms of the glucose unit in cellulose are in the glycol configuration, products other than simple esters may conceivably be formed in the reaction. Paquin [9] heated an equimolar mixture of urea and ethylene glycol for several hours at 150–175° C. and obtained oxazolidone,



If urea reacted with cellulose in this manner, the compound formed would contribute to the fixed nitrogen content of the treated cellulose, would contain blocked 2 and 3 hydroxyl groups thus conferring CED insolubility, and would contain a carbonyl group as required by the infrared spectrum of the treated cellulose. Oxazolidone was prepared according to Paquin and its infrared spectrum was obtained (Figure 7). Although there is a strong absorption at 5.75μ, which is in the vicinity of the 5.85μ absorption of the treated cellulose, there is no peak in the region of 6.2μ. Any absorptions from an oxazolidone-type grouping in the treated cellulose would be completely masked in the spectrum of the urea-treated cellulose, so if any of this grouping is present infrared spectroscopy is not likely to reveal its presence. Another group that could attach through the 2 and 3 hydroxyl groups and have the same effect on the cellulose properties as the oxazolidone compound is that of the ethylene urea type,



When urea is heated together with ethylene glycol under proper conditions, ethylene urea,



is formed. However, to get this product the reaction must be carried out at very high temperatures, up to 240° C., and usually under pressures greater than atmospheric. Since these are not the conditions under which urea and cellulose are reacted, reaction of the 2 and 3 hydroxyl groups with urea in this manner is not considered likely.

Formation of cyamelide in the fiber to give a fixed nitrogen component can be dismissed because this compound would not react with the cellulose to cause insolubility in CED. Furthermore, it is considered to be a linear polymer with no amide grouping present. On boiling with water it gives ammonia and carbon dioxide. A sample of urea-treated yarn which contained 1.85% total nitrogen analyzed for less than 0.10% ammonia nitrogen. Analysis for percent acyl by the modified Eberstadt method showed only 0.3% acyl as carbamate present. It is hardly possible, however, to draw any conclusions, such as degree of substitution and the like, from this analytical data because only a small part of the cellulose has been reacted.

Summary and Conclusions

A reaction occurs between cellulose and urea when cellulose and urea (applied in aqueous solution) are heated to an elevated temperature. Manifestations of reaction are (1) insolubility of the treated cellulose in CED, (2) changed infrared absorption spectrum, (3) nitrogen content unaffected by boiling water, (4) changed dyeing properties, and (5) modified moisture regain.

When cotton celluloses I, II, and III are treated with urea without a catalyst, the total nitrogen content is less than 2%, varying according to the cellu-

lose, while that of viscose rayon is over 3%. Use of a catalyst, cupric chloride, increases these values to 2–3% and to almost 5%, respectively. This indicates that the accessibility of the cellulose is an important factor in the extent of reaction. The X-ray diffraction pattern of the reacted cellulose is the same as that of the untreated material, showing that the reaction is confined to the amorphous region. The properties of the original cellulose are completely restored by boiling the reaction product in 2% caustic solution for 30 min. The application of molten urea to cellulose fails to bring about all the above changes, and total nitrogen content is quite low. In spite of the above changes, however, the textile properties of a cotton fabric treated with aqueous urea solution show little change at all.

The chemical nature of the reaction product is still a matter of speculation, although there is some evidence indicating that cellulose carbamate is the principal product formed. This is based on infrared absorption data and on consideration of the behavior of urea at elevated temperatures. Biuret dissolved in dimethylformamide and applied to cellulose under the same conditions as urea also reacts with cellulose. The reaction product displays the same properties as those of the urea reaction product.

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Comparative Wool Scouring Studies

Part I: Yield and Regain Differences between Solvent and Aqueous Methods

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Abstract

In laboratory trials on samples from individual fleeces solvent degreasing has shown a higher yield than aqueous alkaline scouring. Differences of 0.5% to 1.4% of clean dry fiber are found when solvent degreasing is compared with traditional soap–soda scouring.

Evidence is presented showing that the difference in yield is due to dissolution of oxidized protein material from the tip portion of the wool fiber by hot alkaline scouring solutions.

Regain of scoured wool at standard conditions is found to vary with the method of cleaning. Wool cleaned by solvent or neutral detergent has a lower regain than that from alkaline scouring.

Introduction

Mill trials, comparing solvent degreasing with soap–soda scouring, have indicated [23] a higher total yield of wool obtained from solvent degreasing [28]. Although there has been no previous comparative yield study, the effect of soap–soda scouring on wool has been examined by various workers. It is known that wool may be damaged during soap–soda scouring by excessive alkaline conditions or too great temperature [3, 5, 15, 26, 31, 32]. However, it would appear that, provided temperature does not greatly exceed 50° C. and excessive use of alkali is avoided, soap–soda scouring does not cause significant fiber damage [1, 14, 16, 17, 24]. The present paper describes laboratory experiments designed to obtain further information on the apparent differences in yield observed in the above mill trials.

Experimental

Three experiments were carried out on different types of fleece. In each case the fleece, after conditioning under standard conditions (65 ± 1% RH, 20 ± 1° C.), was divided into samples of 50 g. each. In order to obtain uniform and comparable samples a rotational sampling procedure was adopted in which successive handfuls of staples were taken from different areas of the fleece in rotation. Each handful was then divided among sample bags. Considerable care was taken in this procedure and the technique has proved very satisfactory. Good agreement in yields was obtained for samples treated similarly.

After preparation, samples were scoured in groups by one of the methods below, squeezing procedure in each case being to pass the sample, wrapped in a towel, through backwash squeeze rollers under 4 tons total load.

Solvent Scouring

Solvent treatment was carried out at room temperature by washing each greasy sample for 3 min. with hand agitation in 1 l. of white spirit and repeating the procedure four times. The same procedure was then repeated using four 1-l. water washes at room temperature. After the first and fourth washes, both solvent and water, samples were squeeze rolled, hand wringing being used after the other washes. To avoid fiber loss, the washing solutions in this and all subsequent scouring procedures were always filtered through wire gauze (14 and 20 mesh) and any small fiber pieces collected and returned to the sample.

Simulated Soap–Soda Scouring

To avoid deposition of fatty acids on the wool, the soap in a simulated soap–soda scouring was replaced by a nonionic detergent. The same nonionic detergent was used in other scouring methods below and was a commercial product (100% active) of the alkylaryl polyoxyethylene ether type in which 1 mole of nonyl phenol was condensed with approximately 9 moles of ethylene oxide.

The scouring solution (pH 10.5) contained 0.3% nonionic detergent and 0.12% soda ash. Each sample was treated by hand washing for 3 min. in four successive 1-l. baths of solution at the temperatures 52.5–55°, 50–52.5°, 47.5–50° and 45–47.5° C., respectively. After each wash, samples were squeeze rolled. The pH values of the solutions after washing were generally 9.5, 10.2, 10.3, and 10.4, respectively.

Samples were then treated similarly with three 1-l. water rinses (50–55° C.), hand squeezing after the first two and finally squeeze rolling.

Alkaline Nonionic Detergent Scouring

This method was devised from detergent manufacturers' suggestions for nonionic scouring of merino 64's with the aid of soda ash in the first bowl (mostly to remove free fatty acid material) and common salt as a builder in the second bowl.

Conditions used in four 3-min. 1-l. aqueous washes are shown in Table I. The samples were squeeze rolled after each wash.

Neutral Nonionic Detergent Scouring

This method, based on detergent manufacturers' suggestions, consisted of four 3-min. 1-l. aqueous washes with hand agitation in the solutions shown for this method in Table I, squeeze rolling after each.

TABLE I. Conditions for Nonionic Detergent Scouring

Method	Wash	Temp., °C.	Detergent, %	Soda Ash, %	Salt, %
Alkaline	1	57–59	0.24	0.2	—
Alkaline	2	55–57	0.36	—	0.53
Alkaline	3	52–54	0.18	—	—
Alkaline	4	50	—	—	—
Neutral	1	60–65	0.24	—	—
Neutral	2	54–57	0.6	—	0.5
Neutral	3	50–55	0.15	—	—
Neutral	4	50	—	—	—

Soap and Soda Scouring

Samples were hand-washed for 3 min. in two successive 1-l. solutions containing 0.10% low titer soap and 0.15% soda ash (pH about 10.7) at 55° and 52.5° C., respectively. These were followed by two 1-l. water rinses at 50° and 47.5° C., respectively. Samples were squeeze rolled after each immersion. The pH values of the first two solutions were 9.9 and 10.4 after washing.

After scouring by the various methods, samples were air dried for at least several days, following which loose dirt and vegetable material were removed by careful handpicking. Samples were then vacuum dried overnight at 60–70° C. to constant weight and allowed to condition at 20° C. and 65% RH from which the regain was calculated. Residual grease was ascertained on the conditioned samples by the I.W.T.O. method [18] after which regain was again determined.

Results

As initial experiments on commercial blends of wool gave inconsistent results, it was decided to work with individual fleeces using the sampling technique described above to give uniform samples.

Preliminary studies on 64–70's merino fleeces indicated a yield advantage for the solvent method. In these experiments, solvent degreasing was carried out as above except that squeezing after each wash was by hand-wringing which gave a satisfactory residual grease level of 0.3%. Aqueous alkaline scouring under similar conditions left 5.7% residual grease and only by heavy squeeze rolling were satisfactory levels attained [4, 8]. For this reason, heavy squeeze rolling was used in all subsequent experiments.

Experiment 1

A merino fleece of 64–70's quality, medium weathered and of good length, was used. The original wax content was 26.0%, determined from representative samples and based on conditioned greasy weight.

Samples were scoured in groups of four by the six different scouring methods.

In this experiment, after residual wax and regain determinations, a Soxhlet extraction with absolute alcohol was carried out for 6 hr. and regain again ascertained.

Residual hot-water-extractable material and dirt content were checked as follows in the cases of solvent degreasing and soap–soda scouring. From each conditioned sample a 5.0-g. portion was taken and extracted with distilled water (200 ml.) for 20 min. in a water bath at 55° C. The extract was filtered through wire gauze (24 mesh) to separate fiber from liquid, and 100 ml. of the filtrate was evaporated to dryness in a previously tared flask. From this the hot-water-extractable material in the whole scoured sample was calculated. The pH of the water extract was also measured. Residual dirt in the wool was estimated by digesting the 5.0-g. wool samples in 250 ml. of 10% sodium hydroxide solution by boiling gently for about 5 min. After cooling, the solutions were filtered through previously tared sintered glass crucibles (porosity 1), the crucibles washed with distilled water and dried to constant weight at 105° C. The dirt content of the whole scoured sample was then calculated.

Table II shows a summary of all results obtained in this experiment. Each is the mean of four samples; for yield figures the calculated standard error is also shown in each case.

Experiment 2

A weathered 60–64's merino fleece having 11.1% initial wax content was used in this experiment.

TABLE II. Fiber Yield, Regain and Residual Grease after Cleaning 64/70's Merino Fleece Samples by Various Methods

(Original greasy weight of each sample 50.00 g.)

Scouring method	Dry scoured wt., g.	Conditioned* scoured wt., g.	Regain after scouring, %	Residual grease content, g.	Dry degreased fiber, g.	Clean dry fiber yield, %	Regain after degreasing, %	Ethanol extract, g.	Final regain, %	Hot water extract, g.	pH of water extract	Residual dirt in wool, g.
Solvent	24.84 ±0.07	28.41 ±0.08	14.36	0.05	24.65 ±0.07	49.30	14.53	0.16	14.75	0.15	5.3	0.04
Simulated soap–soda	24.44 ±0.14	28.17 ±0.14	15.27	0.11	24.23 ±0.13	48.46	15.23	0.13	15.59	—	—	—
Alkaline nonionic	24.38 ±0.09	28.06 ±0.11	15.09	0.08	24.24 ±0.09	48.48	15.09	0.13	15.79	—	—	—
Neutral nonionic	24.67 ±0.04	28.33 ±0.05	14.80	0.14	24.48 ±0.04	48.96	14.42	0.14	15.40	—	—	—
Soap–soda	24.57 ±0.07	28.28 ±0.07	15.08	0.12	24.38 ±0.07	48.76	14.76	0.17	15.70	0.13	7.6	0.06

* 20° C., 65% RH.

TABLE III. Fiber Yield, Regain, and Residual Grease after Cleaning 60/64's Merino Fleece Samples by Various Methods

(Original greasy weight of each sample 50.00 g.)

Scouring method	Dry scoured wt., g.	Conditioned* scoured wt., g.	Regain after scouring, %	Residual grease content, g.	Dry degreased fiber, g.	Clean dry fiber yield, %	Regain of clean fiber, %
Solvent	32.37 ± 0.05	36.96 ± 0.06	14.19	0.12	32.25 ± 0.05	64.50	14.00
Soap–soda	31.64 ± 0.09	36.33 ± 0.10	14.82	0.08	31.59 ± 0.09	63.18	14.48

* 20° C., 65% RH.

TABLE IV. Fiber Yield, Regain and Residual Grease after Cleaning 58's Cross-Bred Fleece Samples by Various Methods

(Original greasy weight of each sample 50.00 g.)

Scouring method	Dry scoured wt., g.	Conditioned* scoured wt., g.	Regain after scouring, %	Residual grease content, g.	Dry degreased fiber, g.	Clean dry fiber yield, %	Regain of clean fiber, %
Solvent	32.85 ± 0.04	37.56 ± 0.03	14.33	0.05	32.65 ± 0.03	65.30	14.10
Soap–soda	32.08 ± 0.07	36.87 ± 0.08	14.92	0.04	31.96 ± 0.07	63.92	14.47

* 20° C., 65% RH.

Ten samples were scoured by each of the two scouring procedures, i.e., solvent and soap–soda. In view of its irrelevance, as shown by the results in Experiment 1, the ethanol extraction was omitted.

Figures in Table III are a summary of the mean results for each set of ten samples. The calculated standard error for each set of yield figures is also included.

Experiment 3

In this experiment a weathered cross-bred 58's quality fleece, classed as a good to super combing wool, was used. The original wax content was 11.8%, based on conditioned greasy weight.

The scouring procedures described for Experiment 2 were again followed, ten samples being scoured by each procedure.

Table IV contains a summary of mean results and calculated standard error for each set of samples.

Discussion

Yields

The success of the sampling technique in obtaining uniform samples may be judged from the low standard errors calculated for all yield figures in the three experiments. The yield differences being examined are, by comparison, large. A definite yield advantage, of dry scoured wool, for solvent degreasing is shown in all three experiments. Expressed in terms of residual fiber after scouring and ether extraction, the advantages found and the calculated standard errors of the differences in fiber yield for the solvent process over soap–soda scouring are $0.54 \pm 0.19\%$ for fine merino wool, $1.32 \pm 0.20\%$ for 60–64's merino, and $1.38 \pm 0.15\%$ for the coarser 58's cross-bred type.

Yields vary with the severity of alkaline conditions. Thus in Experiment 1 neutral nonionic emulsion scouring gave only 0.34% lower yield than solvent degreasing. However, neutral nonionic scouring was the least efficient, as indicated by the residual grease content, of the methods compared. Fong has obtained a similar result [10].

Table II also shows yield results for aqueous alkaline scouring procedures, the two methods not involving soap—simulated soap–soda and alkaline nonionic—giving equal yields. These two methods differ only in that the former involves more alkaline baths so that the effect of alkali in reducing yield may be attributable to the action of the initial alkaline solution. Scouring by the soap–soda method gives a yield similar to the simulated soap–soda procedure. The very slight increase is presumably due to deposition of a small amount of soap on the fiber.

It is most probable that the lower scouring yields found for alkaline methods is a result of dissolution by the warm alkaline baths of the oxidized portion of wool occurring near the staple tip [7, 29]. Comparison of Tables II, III, and IV shows that the yield reduction increases with increasing coarseness of wool used. It is well known that coarser wools are particularly subject to damage by sunlight owing to the open nature of the fleece [30] allowing a greater length of the staple to be exposed to weathering than with the finer and denser merino wools.

To test this theory, some of the fleece used in Experiment 1 was divided into tip and base halves and treated as follows. A sample (50 g.) from each portion was solvent degreased as described above, extracted with dry ether to remove residual grease, then conditioned to constant weight. Each was then washed in 1 l. of dilute ammonia (pH 10.5) for 3 min. at 55° C.; this solution was used in place of soap–soda as it would leave no residue on subsequent evaporation. After the wool was removed, the solution was filtered through wire gauze (14 mesh) to eliminate loose fiber and then evaporated to dryness in a previously weighed flask. The dry residues obtained were weighed, hydrolyzed, the hydrolysate dinitrophenylated by Sanger's method [25], and the dinitrophenyl-amino-acids separated by paper chromatography as described by Bradbury [6].

Table V shows the amino acid content of the residues obtained from both tip and base portions, and for comparison Simmonds' [27] amino acid content of merino 64's wool, as weight percentages, are included. The figure for cysteic acid in wool is based on Bradbury's determinations [6]. The results show that the protein material extracted from wool by brief treatment in the dilute alkaline bath has very low cystine and very high cysteic acid content compared with wool. In addition, the aspartic acid content of tip extract is high, the glutamic acid content of base extract is high, glycine content of both tip and base extract is high, and arginine content is low, compared with wool.

From the amino acid analysis it is possible to calculate the percentage protein extracted from tip and base portions. These results are included in Table

TABLE V. Amino Acid Content of Protein Material Extracted from Wool Fiber by Ammonia Solution (pH 10.5 for 3 min. at 55° C.)

Amino acid	Wt. % of amino acid from protein extracted from		Known amino-acid content of merino 64's wool [27]
	Tip	Base	Wt. %
Cystine	0.7	0.4	11.3
Glycine	10.5	17.0	5.0
Alanine	6.4	6.0	3.7
Aspartic acid	11.5	4.3	6.7
Glutamic acid	16.9	33.6	15.0
Serine	11.4	8.3	9.0
Threonine	6.4	3.8	6.6
Proline	5.6	3.9	7.3
Iso-leucine / Leucine / Valine	15.5	12.3	15.7
Lysine	0.9	1.2	2.8
Tyrosine	9.8	5.0	6.4
Arginine	3.4	3.5	10.5
Cysteic acid	1.0	0.6	0.2

TABLE VI. Date Obtained on Solvent Degreasing 50.0-g. Samples of Tip and Base Portion of Merino 64's Wool, Followed by Extraction of Protein Material from the Fiber by Treatment with Ammonia Solution (pH 10.5 for 3 min. at 55° C.)

	Tip	Base
Original grease content	23.55%	24.56%
Wt. after solvent degreasing	27.50 g.	31.09 g.
Residual grease after degreasing	1.48%	0.45%
Clean conditioned degreased fiber after ether extraction	27.10 g.	30.95 g.
Dry residue left after evaporation of ammonia scour solution	1.47 g.	0.22 g.
% protein material in residue from amino acid analysis	11.28%	8.56%
∴ Protein in residue	0.17 g.	0.02 g.
Dissolved protein as % of clean wool washed	0.6%	0.06%

VI which also shows other details of the tip and base experiment. As expected, a higher yield of wool is obtained from the base half, and the tip portion is more difficult to degrease, as shown by residual grease content. Table VI shows that a considerably larger amount of protein material was extracted from the tip portion of the staple by alkaline treatment than from the base, thus confirming that solvent degreasing does not remove from wool oxidized tip material which is readily removed by hot aqueous alkaline solutions. In addition, it is seen that aqueous alkaline treatment removes a small amount of protein from the staple base [33].

Regain

In all three of the yield experiments (Tables II, III, and IV) it is seen that the regain of scoured wool varies with the method of scouring. Moreover the regain generally changes relatively little with removal of residual grease.

The more severe scouring methods apparently cause greater protein degradation resulting in the formation of more polar locations to which water may be bound. The influence of previous treatment on the absorption of water by wool has been briefly discussed previously [2]. It is known that the equilibrium regain of wool is considerably affected by its previous treatment, but the absorption properties can be restored by soaking in water except when chemical action has taken place. In the present study the final treatment for each method of scouring involved a water wash, and the regain differences therefore are due to chemical changes. They are not due to residual surface matter on the fiber since they remain after subsequent solvent extraction.

Because the regain values themselves appeared to be an indication of damage to wool, an attempt was made at the end of the yield and regain sequences to assess damage by solubility in urea-bisulfite [20], as in the comparison of various methods of scouring made by Keppler [19]. This author found nonionic detergent scouring and solvent degreasing to give wool with a urea-bisulfite solubility of 70% compared with 59% for similar wool scoured with soap–soda. In the present work, it was found that all of the samples from various washing treatments had solubilities of about 16%, and subsequently it was established that the urea-bisulfite solubility was sensitive to heat and reduced by the several regain determinations made during the experiment. Gianola, Meyer, and Grillot and also Dusenbury have recently described similar findings [9, 11]. The alkaline thioglycollate test was also previously known to be sensitive to prior heat treatment of the wool sample [21, 22].

Extraction

Results in Table II for ethanol extraction, after ether, show that no significance may be attached to this technique for estimating "residual soap." Thus

although only one scouring method included here involved the use of soap, ethanol extracts for all methods are almost identical. Indeed solvent degreasing, in which no detergent at all is involved, gives an ethanol extract equal to that of wool scoured with soap–soda. Therefore, as suggested by previous research [12, 13, 34], the method is of little practical value.

Acknowledgments

The author wishes to thank Dr. M. Lipson for helpful discussions and Mr. Allan Deacon and Mr. A. J. Maksay for assistance with experimental work. Mr. H. Groll carried out the amino acid analyses.

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Blending Cottons Differing in Fiber Bundle Break Elongation

Part II: Effect on Properties of a Combed Broadcloth

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Abstract

Two control cottons, differing in fiber bundle break elongation, but having other pertinent fiber properties essentially equal, were blended in different percentages, spun into warp and filling yarns, woven into a standard combed broadcloth, and then finished commercially. This report discusses the physical properties of these fabrics. Two cottons having significant differences in fiber break elongation at the fiber stage show very little difference in fabric break elongation after finishing, indicating that the influence of fiber elongation gradually becomes less evident during successive fabric finishing processes. In general, the high elongation fiber cotton produces grey fabric of superior qualities, *viz.*, breaking and tearing strengths, elongation, and flex resistance, when compared with fabric made with low elongation fiber cotton. Furthermore, data also indicate that the values of fabric properties of the blended lots cannot be predicted from those of the controls when the fabrics are subjected to various chemical treatments. This report corroborates other findings that no apparent advantage, from the standpoint of textile quality, exists in blending low and high elongation fibers—whether in blends of natural-natural or natural-synthetic fibers.

Introduction

In a previous report the authors discussed the effect of blending cottons differing in fiber bundle break elongation (henceforth referred to as fiber elongation) on single yarn properties. In this study, a high and a low elongation cotton, along with different percent blends of these cottons were spun into warp and filling yarns, woven into a standard combed broadcloth, and then finished commercially. The purpose of the study was to investigate the effect of cotton fiber elongation on the properties of the fabrics at different stages of processing. This report discusses the physical properties of these fabrics at various stages—grey; bleached; bleached, mercerized, and dyed. The effect of resin treatments applied on these fabrics in this laboratory is also reported.

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

Materials and Methods

In this study a low elongation cotton, Strain No. 330, and a high elongation cotton, Pima S-1, were used. These cottons were processed individually (100%) and in blends of 75%/25%, 50%/50%, and 25%/75%; making a total of five lots. The 100% Strain No. 330 and 100% Pima S-1 were used as control lots. Fiber properties of these cottons shown in Table I were obtained from the finisher picker laps, the first stage in which all common properties can be measured. Efforts were made to observe the changes in the three blended lots in comparison to the controls. Each of the five lots of cotton was combed and spun into warp (60/1, 10 tex, 4.0 T.M.) and filling (60/1, 10 tex, 3.5 T.M.) yarns and then woven into a standard broadcloth ($37\frac{1}{2}$—144 × 76—4.3). These fabrics were finished in a commercial finishing plant except for the resin treatment. They were sewn together to form a continuous length to insure uniform treatment for

TABLE I. Fiber Property Summary *

Fiber property	Cottons				
	100% Strain #330	75%–25%	50%–50%	25%–75%	100% Pima S-1
Grade	2	—	—	—	2
Length					
Classer, in.	$1\frac{3}{8}$	—	—	—	$1\frac{7}{16}$
Suter-Webb					
UQL, in.	1.35	1.32	1.35	1.34	1.33
Mean, in.	1.12	1.10	1.13	1.14	1.13
C.V., %	30	30	29	26	25
Fineness (Suter-Webb)	3.9	3.7	3.7	3.7	3.6
Maturity (sodium hydroxide method), %	89	89	92	90	91
Strength (Stelometer, $\frac{1}{8}$ in. gauge), g./tex	26.4	26.0	26.0	27.1	30.0
Elongation (Stelometer, $\frac{1}{8}$ in. gauge), %	7.2	7.7	8.8	9.5	11.1

* Measurements made on fibers from finisher picker laps.

all lots during chemical processing. Each of these lots is designated by its card sliver fiber elongation value expressed in percent (7.1, 7.8, 8.5, 10.0, and 12.3, see Table II) because card sliver was the first stage in which a good mix was obtained. Addition of resin (Rhonite R-1 [2]) was done in the pilot finishing plant of this laboratory.

Testing Procedure

Fabric breaking strength and elongation-at-break were determined by the strip (1 in.) method, using a pendulum-type tester [1a]. Tearing strength was determined by the tongue method using the Instron [2] tester and integrator. Crimp measurements were determined by the load elongation method using an IP-2 tester [2] [6]. Abrasion was determined by the flexing and abrasion method [1c]. Air permeability was determined with the Gurley Permeometer [2] [1b]. Wrinkle resistance was determined by the Monsanto Wrinkle Recovery Tester [2] [1d].

Results and Discussion

Breaking Strength

Data on fabric breaking strength in the warp direction indicate that the high elongation cotton produces fabric with higher strength than does the low elongation cotton. Furthermore, as in single yarns, if a line is drawn connecting the values for fabric strengths of the control lots, the fabric strengths of the blends all fall below this line. It holds true for fabrics at all stages of processing, as shown in Figure 1. It is significant that this phenomenon already reported [4, 5] in single yarns also occurs with fabrics; blends of two cottons of

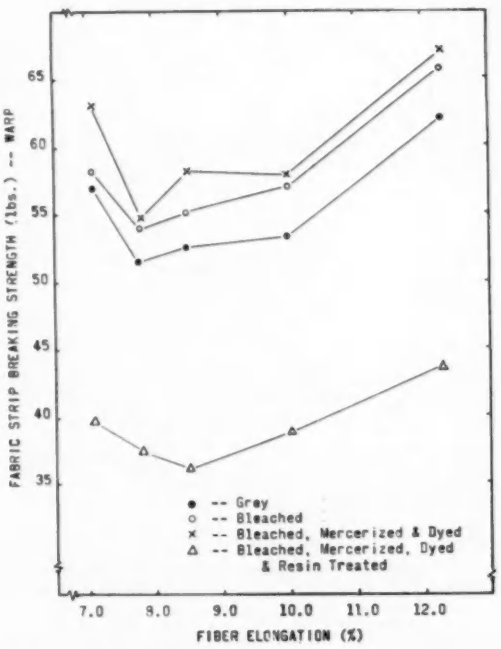

Fig. 1. Effect of differing fiber elongation in cottons on the warpwise strip breaking strength of grey and finished fabrics.

[2] It is not the policy of the Department to recommend the products of one company over those of any others engaged in the same business.

unequal fiber elongation will give lower strength than would be predicted by a simple ratio based on the strengths of the constituents of the blend. Also, the bleached and the bleached, mercerized, and dyed fabrics were stronger than the grey.

In general the fillingwise fabric strengths dropped when the grey fabrics were bleached and when they were bleached, mercerized, and dyed, particularly the 10.0 and 12.3 (75%/25% and 100% Pima S-1) lots, as shown in Figure 2. Except for the bleached fabrics, the fillingwise strengths of the blends fall in between the control lots. The breaking strengths were not adjusted because the thread counts of the five lots were similar in a given stage of fabric processing.

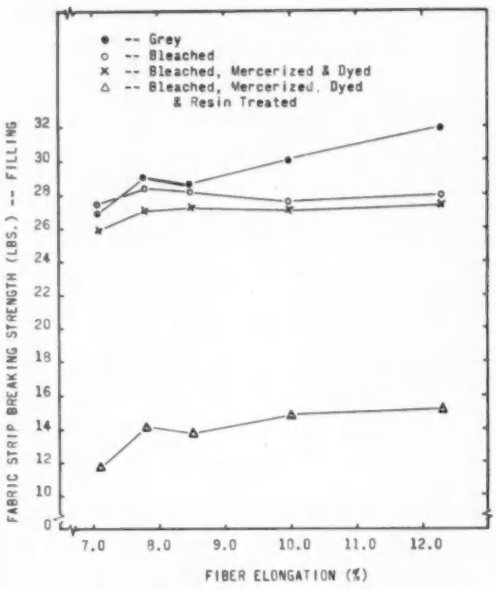

Fig. 2. Effect of differing fiber elongation in cottons on the fillingwise strip breaking strength of grey and finished fabrics.

The different shape of the curves in the case of warp strength and filling strength may be explained as the conjugated strength effect of the warp and filling yarns in the fabrics due to the fabric construction, in which the proportion of warp and filling yarns is about two to one. Apparently, this conjugated strength effect was more prominent in the control cottons than in the blended lots, and the effect in the warp direction more distinct than in the filling direction.

Elongations at Break

Table II shows that the high elongation cotton produces a high elongation fabric, while the low elongation cotton produces a low elongation fabric, with the blends falling in between. This remains true only for the grey and bleached fabrics. The warpwise elongation values in Column 6 show that fabric elongation in the 12.3 lot is still greater than in the 7.1 lot, while the values for the blends are less than for both of the controls, although the differences are relatively small. Also, as the warpwise elongation lessened in each successive process, the fillingwise elongation increased. Furthermore, Figure 3 shows that while there was a 73% difference in fiber elongation between the two control cottons, this percent difference sharply decreased as the fibers were spun into yarns, woven into fabrics, and subjected to successive finishing processes. The chart was plotted on a semilog scale to show the relative magnitude of the changes. The marked decrease in percent difference shows that the differences in fiber elongation are successively diminished during processing, from spinning to chemical finishing.

TABLE II. Effect of Differing Fiber Elongation in Cottons on the Warpwise and Fillingwise Fabric Elongation of Grey and Finished Fabrics

Fiber elongation of controls and blends, %	Fabric elongation, percent					
	Grey		Bleached		Bleached, mercerized & dyed	
	Warp	Filling	Warp	Filling	Warp	Filling
7.1 (control, 100% Strain no. 330)	17.3	7.6	9.8	11.2	7.2	20.5
7.8 (75%/25%)	18.8	7.8	10.4	11.2	6.5	21.2
8.5 (50%/50%)	18.0	8.6	10.0	12.2	7.0	22.8
10.0 (25%/75%)	19.3	8.8	10.3	12.4	7.1	21.1
12.3 (control, 100% Pima S-1)	20.4	9.6	11.0	13.6	7.7	22.9

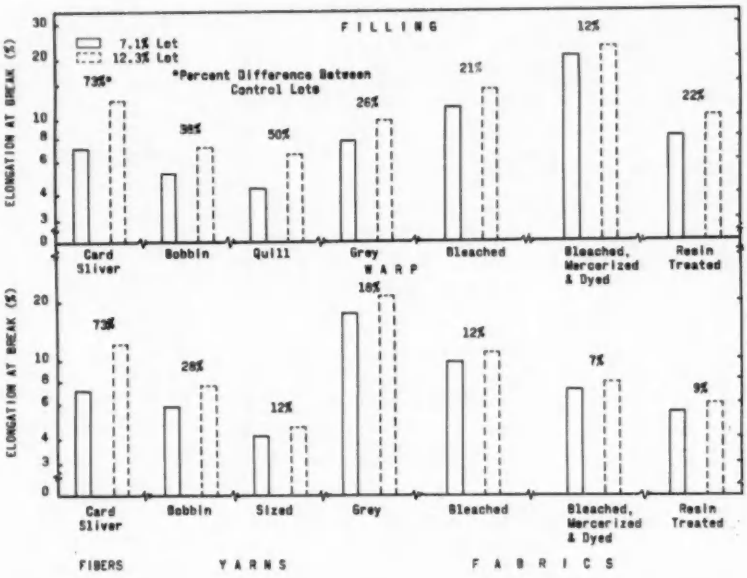

Fig. 3. Percent change in elongation of the control lots in the stages: fiber, yarns, and fabrics (grey; bleached; bleached, mercerized and dyed; and resin treated).

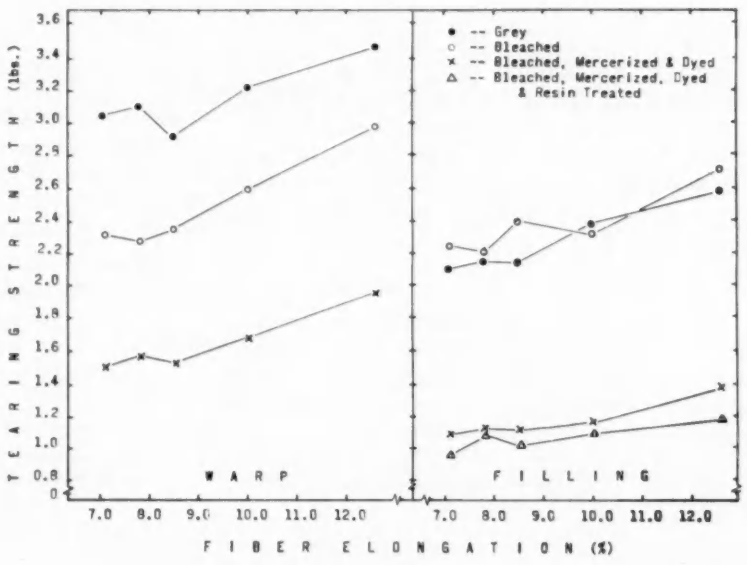

Fig. 4. Effect of differing fiber elongation in cottons on the tearing strength of grey and finished fabrics in warpwise and fillingwise directions.

Tearing Strength

Figure 4 shows that the high elongation cotton fabrics have much higher tearing strength values than the low elongation cotton fabrics. The warp tearing strength values of the blends are lower than those of the 12.3 lot but show no particular trend. The filling tearing strength values of the blends, in general, fall in between those of the two controls. The bleaching process degrades the warpwise tearing strength of the fabric, and mercerizing and dyeing further degrade this fabric property, warpwise as well as fillingwise. In tests of the warpwise tearing strength of the resin-treated fabrics, the fabrics tore across the filling due to unbalanced fabric structure (144×72) and to the apparent great strength differential between warp and filling. Therefore, no

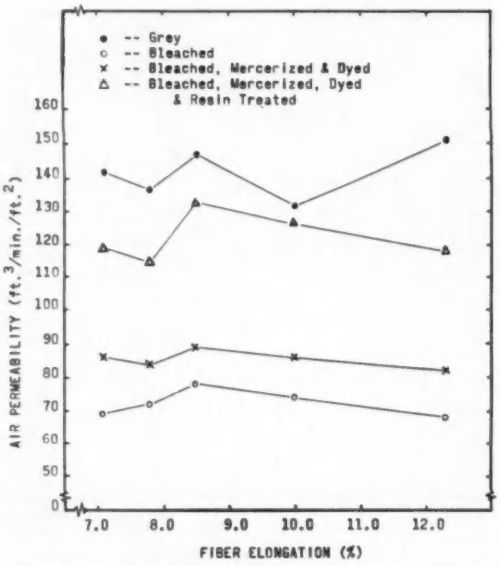

Fig. 5. Effect of differing fiber elongation in cottons on the air permeability of grey and finished fabrics.

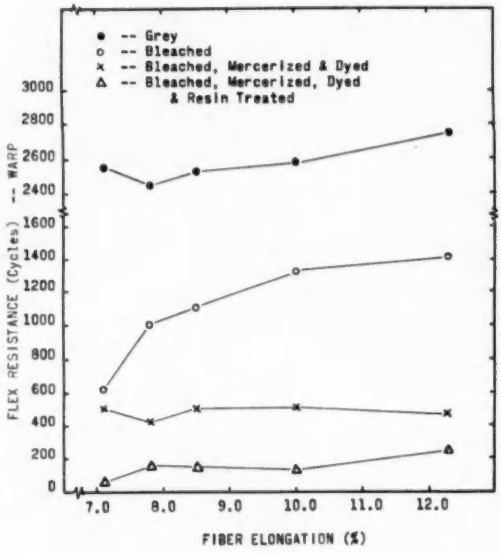

Fig. 6. Effect of differing fiber elongation in cottons on the flex resistance of grey and finished fabrics.

assessment can be made of the warpwise tearing strength. However, fillingwise data show that although in general the slope of the trend line exhibited by the resin-treated fabrics is considerably less than that of the grey fabrics, there is still an appreciable, 21%, difference between the control lots (12.3 and 7.1).

Air Permeability

Chemical finishing also reduces the air permeability of the fabrics, as shown in Figure 5. The bleaching process caused a tremendous drop in air permeability, but the succeeding processes tend to restore some of the porous characteristics in the fabrics. However, no definite trend can be established between fiber elongation and air permeability of the fabric.

Flex Resistance

In general, the 12.3 lot fabric has greater flex resistance values than the 7.1 lot, as shown in Figure 6. This was expected, since the flex resistance value was thought to reflect the toughness of the fabric (toughness being defined as half the product of tenacity and percent elongation at break). However, the flex resistance values of the blends were rather erratic and inconclusive.

Wrinkle Resistance

Table III shows that the wrinkle resistance of the resin-treated fabric increased on an average of about 90% warpwise and 56% fillingwise over fabric not resin treated. The factor of fiber elongation was evidently independent of the resin treatment since the data showed no trend. However, data on the bleached, mercerized, and dyed fabrics (used as controls in this evaluation) indicate that the 12.3 lot fabric has a higher wrinkle resistance value than the 7.1 lot fabric, and that the values for the three

TABLE III. Effect of Differing Fiber Elongation in Cottons on the Wrinkle Resistance of Finished Fabrics

Fiber elongation of controls and blends, %	Wrinkle resistance, degree			
	Bleached, mercerized and dyed		Bleached, mercerized, dyed and resin treated	
	Warp	Filling	Warp	Filling
7.1 (control)	77	85	148	148
7.8	75	90	146	142
8.5	75	95	148	147
10.0	76	96	146	146
12.3 (control)	83	100	148	144

blends fall below those of both control lots in warp but not in filling.

Crimp

Fiber elongation does not affect yarn crimp in the fabric. Yarn crimp in the finished fabrics was much less than that found in the grey fabric. This may be attributed to the stresses imposed on the fabrics during finishing operation. Since the reaction of yarn crimp to finishing operation is similar to that of fabric elongation, crimp data are not shown.

Conclusions

Findings from this investigation indicate that, in general, the high elongation fiber cotton produces fabric of superior qualities, *viz.*, breaking and tearing strengths, elongation, and flex resistance, as compared to fabric made with low elongation fiber cotton.

Data also indicate that the properties of fabrics produced from the blended lots cannot be predicted from those of the controls when the fabrics are subjected to different types of finishes. For instance, the values for fabric strength (warpwise) and for wrinkle resistance were lower for the blended lots than for the controls, whereas the values for fillingwise strength and elongation, warpwise elongation, tearing strength, air permeability, and flex resistance were rather erratic and unpredictable in the blends.

The wrinkle resistance properties of the control fabrics and the blends were similar after resin treatment but other fabric properties retained their relative levels.

This report corroborates other findings [2, 3, 4] that there is no apparent advantage, from the standpoint of textile quality, in blending low and high elongation fibers—whether in blends of natural-natural or natural-synthetic fibers.

Acknowledgment

The authors wish to express their appreciation to all the members of the Product Evaluation Investigations of the Southern Utilization Research and Development Division, particularly to McLean George, J. C. Oubre, and T. B. Murtagh for testing the fabrics and to N. P. Roddy and M. J. Bocage for weaving the fabrics. Special acknowledgment is due J. M. Cheatham, President of the Lowell Bleachery South, Griffin, Georgia, and his associates for commercially finishing the experimental fabric used in this study.

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Letters to the Editor

A Vibroscope to Measure the Counts of Fibers in Place on the Dynamometer

Société Rhodiaceta
Service d'Etudes Physiques
45, Rue du Sergent Michel-Berthet
Lyon, France
November 14, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The vibroscope method is used more and more to determine the counts of individual fibers. Very often these determinations are carried out with a view toward a dynamometric reading. First the equipment is set up and then each one of the fibers to be examined is measured on the vibroscope. They are then placed and tested one by one on the dynamometer. Thus for each fiber it is necessary to carry out two operations, both of which are delicate and time-consuming (especially for the fine counts). The amount of time required could be cut down considerably if the reading of the yarn count could be carried out with the fiber already in position on the dynamometer and ready to undergo the tensile test.

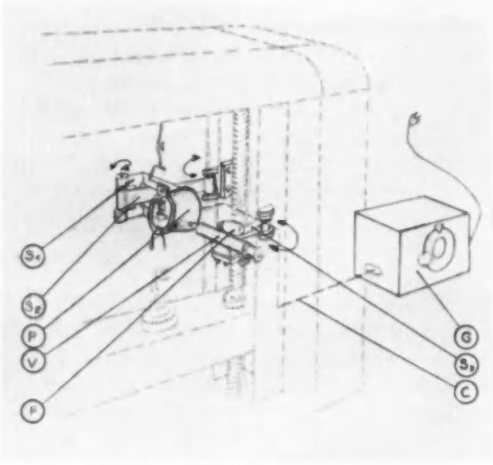

Fig. 1. General view of the apparatus adapted to the Instron dynamometer.

With this purpose in mind, a special kind of vibroscope was developed in order to determine the count of the fiber without removing it from the dynamometer. To achieve this, only one part of the vibroscope is fastened on the dynamometer. It is brought close to the fiber very rapidly, exactly at the moment when the count is to be determined, without any adjustment being necessary. It is then removed in a minimum of time without hindering the carrying out of the dynamometric test. Below we describe the apparatus as adapted to the Instron dynamometer. However, it can be adapted to any type of dynamometer by means of simple changes.

Principle and Construction of the Apparatus as a Whole

We know, according to the principle of vibrating strings, that when a fiber of length L supposedly without stiffness is held at both ends under tension T and has a natural frequency of transversal vibrations f_1, its mass per unit of length is given in CGS units by:

$$m = \frac{T}{4L^2 f_1^2}$$

The method chosen here for the determination of m consists of keeping L and T constant and varying the frequency of excitation f continuously until we find f_1. This principle has already been used by different authors [1, 2, 4] and is mentioned among others by the ASTM [3]. As we will see later, we believe that it makes it possible to reduce the time required for the determination of yarn counts while maintaining very good accuracy.

The entire equipment is presented in Figure 1 and consists of the following:

1. An excitator of transversal vibrations or "transducer," P, which is to come into mechanical contact with the fiber to be measured and functions on the electrodynamic principle.

2. Attachments S_1 and S_2, which serve as supporters on the dynamometer. They are fashioned in such a way that the transducer can be rapidly brought into contact with the fiber and quickly re-

moved. When removed the unit does not in any way alter the normal functioning of the dynamometer.

3. A generator of sinusoidal electrical signals of variable frequency, operating continuously to feed transducer P. In Figure 1 the generator is designated by G and is connected to the transducer by cable C.

4. A microscope V, for observation of the fiber. The fiber is illuminated by means of a small projector, p, attached to the microscope.

5. Both the projector and the microscope are supported on the dynamometer by support S_3 which also is made in such a way that the entire unit can be put into position rapidly and removed rapidly at the exact moment of measuring. For routine, it is possible to focus the microscope in one setting for all of the measurements by means of an appropriate system of notches.

In Figure 1 the Instron dynamometer is drawn with broken lines while the vibroscope is drawn with solid lines. The arrows indicate the movements of the supports of the vibroscope necessary to put it into position or to retract it.

Detail Description of the Transducer, the Fiber and the Microscope

The left part of Figure 2 illustrates the placing of the fiber on the dynamometer: the fiber (1) has a spring-clip attached to its lower end (2) so that it hangs under tension T. The upper end is held in the jaws (3) of the dynamometer.

The right side of Figure 2 shows the same fiber after the transducer (5) was brought into contact with it. The fiber is no longer vertical but is described by the broken line A-B-C-D. This is due to the presence of a small tongue (6) which is held firm and a movable tongue (4) which constitutes the exterior vibrating part of the tranducer. The two edges B and C of the tongues are perpendicular to the fiber with B a little further back than C (approximately 0.5 mm.). They define the vibrating length L of the fiber. Between the two tongues, tension T of the spring-clips (2) prevails. On resonance we can observe the "spindle" between these two tongues.

This set-up makes it possible to maintain L and T constant from one fiber to the next without operator's intervention. These values are previously determined once for all. Length L is normally set up at 20 mm. (an appropriate value for the study of fibers 40 mm. or more in length); but for shorter

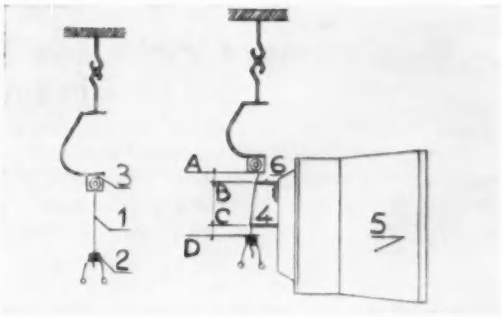

Fig. 2. Detailed views of the transducer and the fiber.

fibers, L can be set up at 15 mm. or 10 mm. by moving the tongue (6) downward. In this case the axis of the transducer (5) can be raised.

The spring-clips which apply tension T to the fiber are made of hardened steel or beryllium bronze with different diameters depending upon the desired weight. It is also their function to transmit to the fiber a certain pre-tension necessary for the dynamometric test. If the spring-clips are used for fiber count measurements on fibers of the same lot, the values determined for f_1 remain within the same order of magnitude since length L is constant. This procedure results also in time saved in resonance frequency tuning.

Finally, the optical axis of the microscope, as indicated in Figure 1, is situated on a plane passing through the center of the fiber. It can also be adjusted in height.

In conclusion, the use of this equipment adapted to the dynamometer results in a large saving of time compared to the usual method in which the fiber count measurement and the dynamometric measurement are made completely separately. Furthermore, the results and the precision of the method are similar to those of usual vibroscopes. By a simple adaptation of the supports, such a vibroscope can be attached to any kind of dynamometer.

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PIERRE DEPALLE

Separations of Methylated Sugars by Gas Liquid Partition Chromatography

Courtaulds, Inc.
Post Office Box 1025
Mobile, Alabama
November 30, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The recent publications [1, 2] on gas-liquid partition chromatographic separations of methyl glycosides of methylated sugars promise great additional sensitivity in the study of polysaccharide derivatives. In the two references cited there is indication that some contradiction exists as to the ability of polyester stationary phases to provide sufficient resolution. We would like to report some experiments which resolve this contradiction, and in addition, report the resolution of some methyl glycosides of dimethyl glucose.

The experiments were performed on three mixtures and six characterized methyl glucosides. The instrument was a Wilkens Aerograph[1] (Model A-100) using a butanediol succinate column (Craig) and two different diethylene glycol succinate [DEGS] columns; all packings were commercial material from Wilkens. The column temperatures used were 150° C., 170° C., and 220° C.; the inlet pressure was 15 lb./sq. in.; helium flow 100 ml./min., and the filament current 200 m amps.; flow rates were measured with a soap-bubble meter. The retention volume of the arbitrary standard methyl 2,3,4,6,-tetra-O-methyl-α-D-glucopyranoside was uncorrected for the pressure drop through the column.

Sample A: Methyl-α-D-glucopyranoside was methylated with a reduced quantity of MeI to yield a mixture of methyl-α-D-glucopyranosides of varying methyl substitution [3].

Sample B: A fully methylated rayon [4] was hydrolyzed in 1.0 *N* methanolic HCl at reflux leading directly to the substituted methyl glucopyranosides and furanosides.

Sample C: α-D Glucose was methylated with a reduced quantity of Me_2SO_4 and NaOH [5] leading to a mixture of both α and β anomers of partially methylated methyl glucosides.

The retention volumes of the standard (methyl 2,3,4,6,tetra-O-methyl-α-D-glucopyranoside) and the relative retention volumes based on the latter are tabulated below. The assignment of the standard and its β anomer was made through known samples. The trimethyl ethers were assigned through the data of Bishop [1]. The dimethyl ethers, where assigned, were identified by running known glucosides.

The paper by Kirchner [2] reporting separations at $> 200°$ C. indicates a lack of resolution on polyester packings. This is in contrast to the paper by Bishop [1] who reported satisfactory separations on the same type of packing at 150° C. The tabulation below indicates that the trimethyl glucosides can be separated satisfactorily at the lower temperatures, but that increasing temperatures cause a rapid aggregation of the relative retention times. This is more pronounced with the "faster" DEGS columns; the latter, however, offer the possibility of identifying the various dimethyl ethers of methyl glycosides.

The difference between the two DEGS columns, I and II, is not well established. The "faster" of the two (I) is nominally a 25% polyester packing which was used extensively for fatty acid ester analysis and is suspected of having lost considerable stationary phase through attrition.

We are in hopes that the separation of dimethyl ethers of methyl glucosides will aid in the elucidation of cross-linking of cellulose.

[1] Wilkens Instrument and Research, Inc., Walnut Creek, California.

Acknowledgment

We would like to thank Dr. John J. Willard, Cellulose Research Institute, Syracuse, New York; Dr. C. T. Bishop, National Research Council, Ottawa, Ontario; and Dr. A. M. Dowell, Buckeye Cellulose Corporation, Memphis, Tennessee for making available to us several characterized methyl glucosides.

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TABLE I

Samples and components*	Relative retention times								
	150° C.			170° C.			220° C.		
	Craig	DEGS2	DEGS1	Craig	DEGS2	DEGS1	Craig	DEGS2	DEGS1
Mixture A									
2,3,4,6 Tetra α P	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2,3,4, Tri α P	2.11	2.34	2.18	1.95	2.52	2.08	1.91	1.69	1.84
3,4,6 Tri α P	2.61	2.89	2.66	2.32	3.53	2.47	2.23	2.29	2.18
2,3,6 & 2,4,6 Tri α P	3.52	3.90	3.68	2.92	3.87	2.96	2.64	3.18	2.59
? Di α P	—	—	—	—	5.49	5.43	3.93	4.02	3.90
4,6 Di α P	—	—	—	—	—	(7.41)	4.58	4.90	4.90
2,3 Di α P	—	—	—	—	—	—	—	—	6.40
? Di α P	—	—	—	—	—	—	—	—	7.90
? Di α P	—	—	—	—	—	—	—	—	11.00
Mixture B									
2,3,4,6 Tetra β P	0.70	0.69	0.75	0.73	0.71	0.65	0.79	0.77	0.72
Unidentified (possibly Tetrameth. Furanoside)	0.89	0.87	—	0.89	0.87	0.79	0.88	0.86	—
2,3,4,6 Tetra α P	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Unidentified	1.28	1.42	—	1.35	1.45	1.15	1.40	1.46	1.40
2,3,6 Tri β P	2.50	2.70	2.19	2.34	2.84	1.98	(2.02)†	(2.52)‡	(2.18)†
2,3,6 Tri ? F	2.93	3.21	(2.94)‡	2.71	3.25	(2.53)‡	(2.15)		(2.30)
2,3,6 Tri α P	3.27	3.84		3.10	3.90		2.56	3.02	2.67
Mixture C									
2,3,4,6 Tetra β P	0.70	0.69	0.66	0.67	0.71	0.71	0.80	0.70	—
2,3,4,6 Tetra α P	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	—
2,3,4, Tri β P	1.80	1.98	1.68	1.75	1.55	1.40	1.75	—	—
2,4,6 Tri β P	(2.38)†	(2.66)†	(2.12)‡	(2.25)†	(2.76)‡	(2.02)	(2.02)†	(2.44)‡	—
2,3,6 Tri β P	(2.45)	(2.84)		(2.36)			(2.16)		—
2,3,6 Tri α P	3.44	3.86	—	3.14	3.92	—	2.58	3.22	—
Characterized Sugars									
2,3 Di β P	—	—	—	—	—	—	—	—	5.30
2,3 Di α P	—	—	—	—	—	—	—	—	6.66
4,6 Di α P	—	—	—	—	—	—	—	—	4.92
4,6 Di β P	—	—	—	—	—	—	—	—	6.10

* Abbreviation is based on Methyl 2,3,4,6 Tetra-O-methyl-α-D-glucoPyranoside.

† Bracketed values indicate poor but clearly indicated resolution.

‡ Values between lines indicate no distinct resolution.

TABLE II. Retention Volume of Methyl 2,3,4,6-Tetra-O-Methyl-α-D-Glucopyranoside

Temperature	Craig	DEGS II	DEGS I
150° C.	2760	1930	395
170° C.	1200	930	184
220° C.	249	215	58

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Elias Klein
Charles J. Barter, Jr.

The Effect of an Airborne Soil on the Photochemical Degradation of Nylon

Department of Nutrition and Home Economics
University of California
Berkeley 4, California
December 1, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The effect of an airborne soil on the photochemical degradation of a nylon yarn has been studied. This airborne soil, similar to soil that might accumulate on textiles during use, was found to accelerate the photochemical degradation of a cotton yarn [2]. As in the earlier study [2], soiled and unsoiled yarns have been exposed to a carbon arc light source. The effects of aging without light and of heat without light on soiled and unsoiled nylon yarns have also been determined.

Bright, type 300, nylon 66 yarn was used, denier 210, F 34, Z 0.75. All yarn samples were prepared for soiling and exposure in a manner similar to that previously described [2]. Yarn samples were soiled by tumbling 5 min. at room temperature in a Launderometer in standard glass containers containing 0.35 g. airborne soil. The yarn samples retained 5% soil by weight, as did cotton samples used in the earlier work. Control yarn samples were tumbled in the same manner but without soil. One set of soiled and unsoiled yarn samples was exposed in a Fade-Ometer, and another similar set aged in darkness under standard atmospheric conditions. A third set was heated in a circulating air oven at 63° C., the mean operating temperature of the Fade-Ometer. Samples were evaluated after 160- and 320-hr. periods. All yarn samples, both soiled and unsoiled, were thoroughly cleaned before evaluation for degradation. Each sample was rinsed twice in distilled water, dipped by hand for 1 min. in 0.1% neutral soap solution at 37.8° C., and rinsed 4 times in distilled water. The soiling and laundering procedures did not significantly affect the strength of the original nylon yarn.

Yarn breaking-strength measurements were made on a constant-rate-of-load type instrument, with the clamps set 3.00 in. apart. The mean of 20 specimens from each experimental group is reported in Table I. The significance of the differences between mean values was determined by calculating the standard error of the difference between two means [1].

TABLE I. Nylon Yarn Breaking Strength, g.

Treatment	160 hr.		320 hr.	
	$\bar{X}$	σ	$\bar{X}$	σ
Fade-Ometer exposure				
Soiled	414	60	205	33
Unsoiled	529	50	272	25
Aged				
Soiled	1381	97	1426	102
Unsoiled	1422	98	1412	85
Heated				
Soiled	1389	100	1415	105
Unsoiled	1386	106	1423	83
Original	1401	137		

Breaking-strength results indicate that the airborne soil accelerated the photochemical degradation of the nylon yarn. The soiled yarns had a greater loss in strength than the unsoiled yarns after 160 and 320 hr. of exposure in the Fade-Ometer; these differences were 22 and 24% respectively. A corresponding difference in strength between soiled and unsoiled yarns was not found to result from aging or heating.

Fade-Ometer exposure caused a pronounced reduction in the breaking strength of the nylon yarns. However, the yarn samples subjected to heat and aged in darkness did not differ significantly in breaking strength from the original yarn.

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MARY ANN MORRIS
BARBARA W. MITCHELL

The Reaction of Dimethylol Urea with Cotton

Textile Research Laboratory
Rohm and Haas Company
Philadelphia 37, Penna.
December 2, 1960

To the Editor:
Textile Research Journal

Dear Sir:

Mehta and Mehta, in their paper on the reaction of dimethylol urea with cotton [3], do not use the methylol formaldehyde determination of de Jong [2] which we adapted for use on resin-treated fabric [5] and which they claim to have used. Since formaldehyde is unstable in 0.5 *N* NaOH, a necessary part of this procedure is the addition of cyanide directly to the hydrolysis medium so that the formaldehyde reacts with it immediately. The necessity for this is demonstrated in Figure 1, where the stability of formaldehyde at a concentration representative of that present in our determinations is compared for solutions in distilled water and in 0.5 *N* NaOH. Since Mehta and Mehta did not add cyanide to the hydrolysis medium, we believe that their data are open to suspicion. Loss of formaldehyde by the Cannizzaro reaction would give them low results for methylol formaldehyde and perhaps account for the difference between their results and ours.

It should further be pointed out that Mehta and Mehta did not examine the catalyst that we studied. We think it not unreasonable to believe that different catalysts or different catalyst levels give reaction products of somewhat different structure, probably depending on the degree and amount of acidity present. We have noticed indications that this may be so [4]. Comparison of catalysts at different arbitrary concentrations, as Mehta and Mehta have done, must be supplemented by concentration studies to throw further light on this difficult problem.

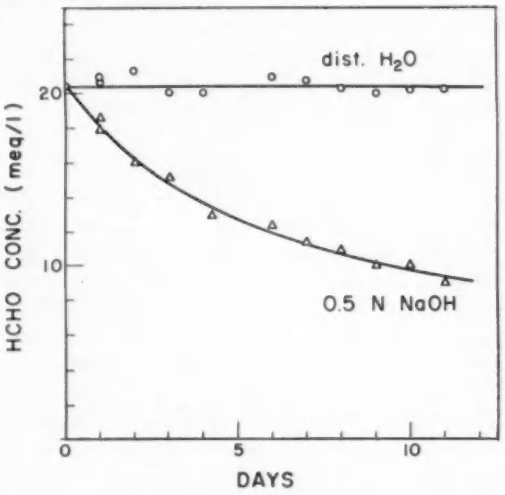

Fig. 1. Stability of formaldehyde solutions in water and 0.5 *N* NaOH at 21° C. The formaldehyde content was determined by the chromotropic acid method [1].

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Richard Steele

Factors Affecting the Amount of Liquid Held in a Fiber Bundle by Interfiber Capillarity

Pfeiffer College
Misenheimer, North Carolina
December 21, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

A fiber bundle will support cusp-shaped liquid columns whenever the liquid-to-fiber contact angle is less than 90° and so long as forces tending to remove the liquid are not greater than than forces tending to preserve the configuration of the liquid–air interface. Hence, the amount of liquid held by interfiber capillarity will depend upon the liquid–fiber contact angle, the radius of the fiber, and the radius of curvature of the liquid–air interface. Preston and Nimkar [1] described the case for contiguous fibers. It is of interest, however, to consider an extension of this development to the case where fibers may be constrained so that the surface tension of the liquid is insufficient to draw fibers into contact at all points, thereby leaving gaps between parallel fibers.

The purpose of this analysis is to express the quantity of liquid supported by interfiber capillarity as a function of the three variables mentioned previously and of a fourth variable, the distance of fiber separation.

An idealized case is represented by the geometric construction in Figure 1 in which perfect cylinders of radius r_1 are arranged in a close-packed configuration, each cylinder with six nearest neighbors, and separated by a distance 2δ. The radius of curvature, r_2, of the liquid–air interface and the liquid–solid contact angle, θ, complete the set of four variables upon which the volume of retained liquid depends. The shaded area in Figure 1 represents $\frac{1}{12}$ of the cross-sectional area of retained liquid associated with each cylinder cross-section in this close-packed configuration. Hence the ratio of liquid volume to fiber volume, Ω, is

$$\Omega = (\text{shaded area}) \frac{12}{\pi r_1^2} \tag{1}$$

Further examination of Figure 1 yields the geometric relations:

$$2\ (\text{shaded area}) = \psi(\delta + r_1) - r_2^2\beta - r_1^2\left(\frac{\pi}{2} - \alpha\right) - r_1 r_2 \sin(\pi - \theta) \tag{2}$$

$$\theta = \alpha - \beta \tag{3}$$

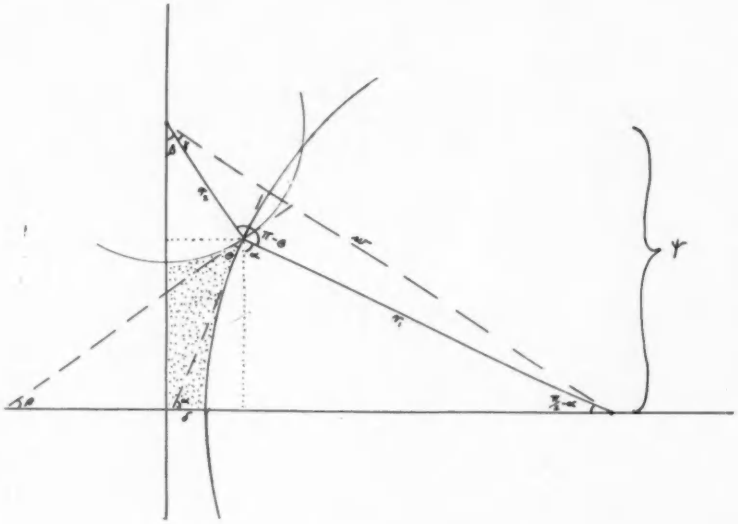

Fig. 1. Geometric construction for deriving $\Omega = f(\rho, \sigma, \theta)$. r_1 = radius of fiber; r_2 = radius of curvature of liquid–air interface; θ = contact angle; $\delta = \frac{1}{2}$ distance of fiber separation. $\rho = r_2/r_1$; $\sigma = \delta/r_1$; $\Omega = 12/\pi r_1^2 \times$ [shaded area] = ratio of liquid volume to fiber volume with close-packed fiber configuration.

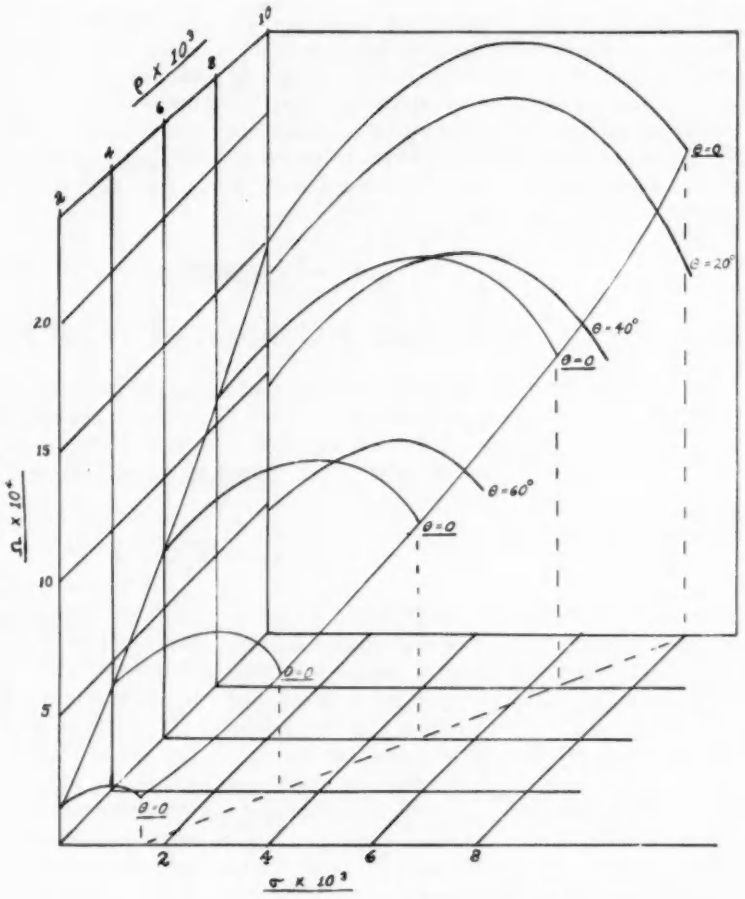

Fig. 2. The relative volume, Ω, of retained liquid in an assembly of close-packed cylinders as a function of (a) the radius of curvature, ρ, of the liquid–air interface relative to the cylinder radius, (b) one half the distance of cylinder separation, δ, relative to the cylinder radius, and (c) the liquid–solid contact angle, θ.

$$\beta = \tan^{-1}\frac{r_1 + \delta}{\psi} - \sin^{-1}\frac{r_1 \sin\theta}{w} \qquad (4)$$

$$\psi^2 + (r_1 + \delta)^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos(\pi - \theta) = w^2 \qquad (5)$$

A reduction in the number of variables required to express $\Omega = \Omega(r_1 r_2, \delta, \theta)$ may be realized by introducing relative dimensions for the distances r_1, r_2, and δ. Letting $\rho = r_2/r_1$ and $\sigma = \delta/r_1$, and combining Equations 1 through 5 we obtain:

$$\Omega(\rho, \sigma, \theta) = \frac{6}{\pi}\left\{(\sigma + 1)\mu + \theta - \rho\sin\theta + (1 - \rho^2) \times \left[\tan^{-1}\frac{1 + \sigma}{\mu} - \tan^{-1}\frac{\sin\theta}{\rho + \cos\theta}\right]\right\} - 3 \qquad (6)$$

where $\mu^2 = \rho^2 + 2\rho\cos\theta - 2\sigma - \sigma^2$. Equation 6 fits the boundary condition that $\Omega \to \frac{2\sqrt{3}}{\pi} - 1$ as $\theta \to 0$, $\sigma \to 0$, $\rho \to 1$, which is the volume of void space relative to cylinder volume in an assembly of close-packed parallel cylinders.

When a fiber assembly is equilibrated with a fixed partial pressure of a volatile liquid, our capacity to calculate the quantity of liquid retained by interfiber capillarity depends upon our knowledge of ρ, σ, and θ. The contact angle, θ, is measured in a forthright manner. The value of ρ can be determined with the aid of the relation

$$ln\frac{P}{P_0} = \frac{v}{RT}\frac{2\gamma}{r} \qquad (7)$$

where P_0 is the vapor pressure over a plane surface, P is that over a surface having a radius of curvature r, v/RT is the molar volume of the liquid divided by the product of the ideal gas constant and the Kelvin temperature and r is the surface tension.

Although a precise value of fiber separation, 2δ, does not appear to have any real significance in a practical situation, we can infer the following. As an ideal close-packed fiber arrangement is distorted so that the average value of fiber separation along the bundle increases, the initial effect thereof is an increase in the volume of liquid retained (Figure 2). Further, it can be predicted that there exists an optimum crimp in continuous-filament yarns for which the volume of interfiber liquid cusps is a maximum for a particular set of atmospheric conditions.

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J. R. KUPPERS

The Sulfur Content of Wool Keratin

Department of Textile Industries
Institute of Technology
Bradford, Yorkshire, England
December 21, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Although the sulfur content of wool is known to vary with quality, analyses of a given quality, e.g., 64's, have been reported over the range 3% to 4%, the majority of values lying between 3.3% and 3.6%. Although small differences may occur from sheep to sheep [9], there is no doubt that the problem of determining the best value for the sulfur content of a given quality of wool is fundamentally one of analysis.

The majority of methods used for determining the sulfur content of wool involve wet oxidation to sulfate ions and the determination of the latter gravimetrically as barium sulfate. The difficulty of this procedure is that the weight of the precipitate of barium sulfate depends on a number of factors, e.g., the time taken for the oxidation of the wool [2] and that taken for the aggregation of the barium sulfate [6]. These times are often arbitrarily fixed, it being reported that deviations give "high" or "low" results. The addition of potassium dichromate to the frequently used nitric-perchloric acid mixture to oxidize the wool has certain advantages, but these are offset by the fact that, probably due to co-precipitation, the weight of the barium sulfate precipitated is dependent on the quantity of dichromate used [6].

In view of the excellent results known to be given by the Schöniger method for determining sulfur in organic compounds [8, 7, 4], which involves burning the material in oxygen in a flask containing hydrogen peroxide and determining the sulfuric acid produced, this method has been applied to 64's wool with the following results:

Percent sulfur, 3.30, 3.32, 3.35, 3.35, 3.28. Mean $= 3.32 \pm 0.01\%$.

Analyses were carried out as described by Macdonald [5], the weighing of the barium sulfate being avoided by using the Wagner technique [11] of titrating with barium perchlorate in isopropanol to a thorin end-point.

A fundamental difficulty of wool chemistry is the lack of correlation between sulfur content and the content of the sulfur-containing amino acids, cystine and methionine. The latter is present to the extent of only 0.6%, corresponding to 0.13% sulfur, so that within wide limits the accuracy of its determination is not important in relation to the elementary sulfur content of wool. The cystine content of wool, however, like the sulfur content, varies with the analytical method employed. Thus, values for 64's wool vary from 10.3% using ion-exchange resin chromatography to 12.3% by Shinohara's method [1]. The former method is known to be unsatisfactory for this amino acid [10]. Recently Lewis, Robson, and Tiler [3] have found a number of sulfur-containing compounds, in addition to methionine and cystine, in wool hydrolysates. In view of the fact that most of these are probably derived from cystine and are Shinohara-positive, the Shinohara method is probably as accurate as any at present available for determining the cystine content of wool, and for 64's wool this value corresponds to 3.28% sulfur. The cystine and methionine contents thus agree with the sulfur content, as determined by the Schöniger method, within 3%.

It is of interest that Myers [6], who meticulously investigated all the variable factors involved in the nitric-perchloric-dichromate method for oxidizing the sulfur of wool to sulfate, has produced a very similar result to that now reported, but the advantages of the much simpler Schöniger method are obvious.

The author wishes to thank Mr. A. T. Masters of the British Rayon Research Association, Manchester, who performed the sulfur analyses.

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Book Reviews

Amino Resins. John F. Blais. New York, Reinhold Publishing Corporation, 1959. 232 pages. Price $4.95.

Reviewed by James P. Shelley, Rohm & Haas Company Research Laboratories, Philadelphia, Pa.

Mr. Blais's treatment of the so-called amino resins is a creditable work in that he has done a reasonably thorough job of covering the various fields of application in which these resins are currently used and this, apparently, is the primary objective of the book. Included are such uses as paper and textile treatment, surface coatings, adhesives, laminating, molding compounds, etc. The book is semi-technical in its treatment of the various applications and contains only a very minimum of chemistry in order to make easier reading for the individual with a non-chemical background. In this regard the author has done a bit overboard, several of the reactions or reaction products being boiled down to highly over-simplified forms.

The coverage of any one field is a rather condensed one and for this reason the book would probably be of value only to a newcomer to the field. The treatment of textile applications is no exception in this respect. If the reader is interested in obtaining a rather broad and generalized picture of the various types of textile applications in which these resins are used, this book will serve the purpose quite well. Beyond that, however, the information contained therein is too deficient in details to be of much value.

Properties and Structure of Polymers. Arthur Tobolsky. New York, John Wiley and Sons, Inc., 1960. Price $14.50.

Reviewed by Robert Ullman, Polytechnic Institute of Brooklyn

This book contains a lucid summary of areas relevant to the work of Tobolsky and his collaborators, mainly dealing with the mechanical behavior of high polymers as understood from stress relaxation studies. Most other polymer properties are treated briefly or not at all.

It is a pity that the author and/or publishers chose this title. The author's intention was apparently much more restricted.

Tobolsky has deliberately avoided a complicated mathematical treatment. The book may be read with profit by graduate students and professional chemists interested in this field.

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In the June Issue

Comparison of Ultraviolet Light Absorbers for Protection of Wool against Yellowing. *W. Gordon Rose, Mayo K. Walden, and Joseph E. Moore*

Some Properties of Continuous-Filament Yarn. *Witold Żurek*

Variation of Cotton Fiber Properties with Length Group. *K. P. R. Pillay and K. S. Shankaranarayana*

The Migration of Liquids in Textile Assemblies. Part IV: Penetration of Fabrics by Liquids. *F. W. Minor, Anthony M. Schwartz, L. C. Buckles, E. A. Wulkow, Melvin P. Marks, and George H. Fielding*

Wearing Qualities of Selected New Mexico Wools. Part I: Strength and Elongation. *Julia Southard Lee, Helen F. Barbour, and Morris D. Finkner*

Quantitative Investigation of the X-Ray Diffraction Picture of Some Typical Rayon Specimens. *P. H. Hermans and A. Weidinger*

Quantitative Evaluation of the X-Ray Diffraction of Ramie Fiber. *P. H. Hermans and A. Weidinger*

Effects of Tension During Resin Treatment on Physical Properties of Cotton Fibers and Yarns. *Rollin S. Orr, Albert W. Burgis, and James N. Grant*